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DEPARTMENT OF THE ARMY PESTICIDE MONITORING PROGRAM, EVALUATION--ETC(U)
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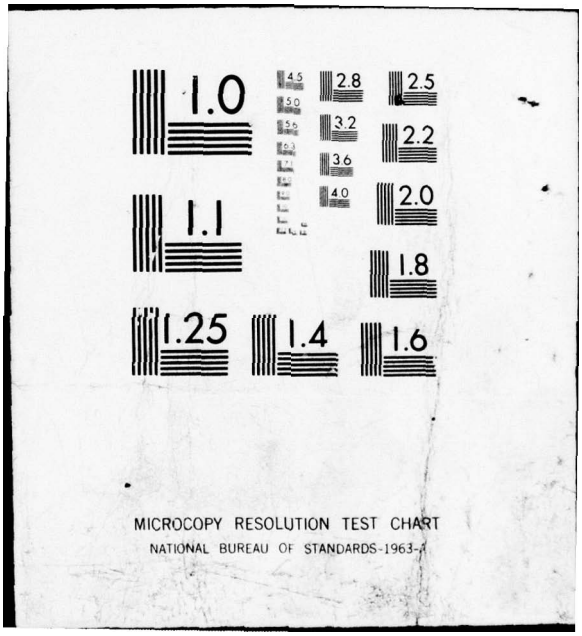
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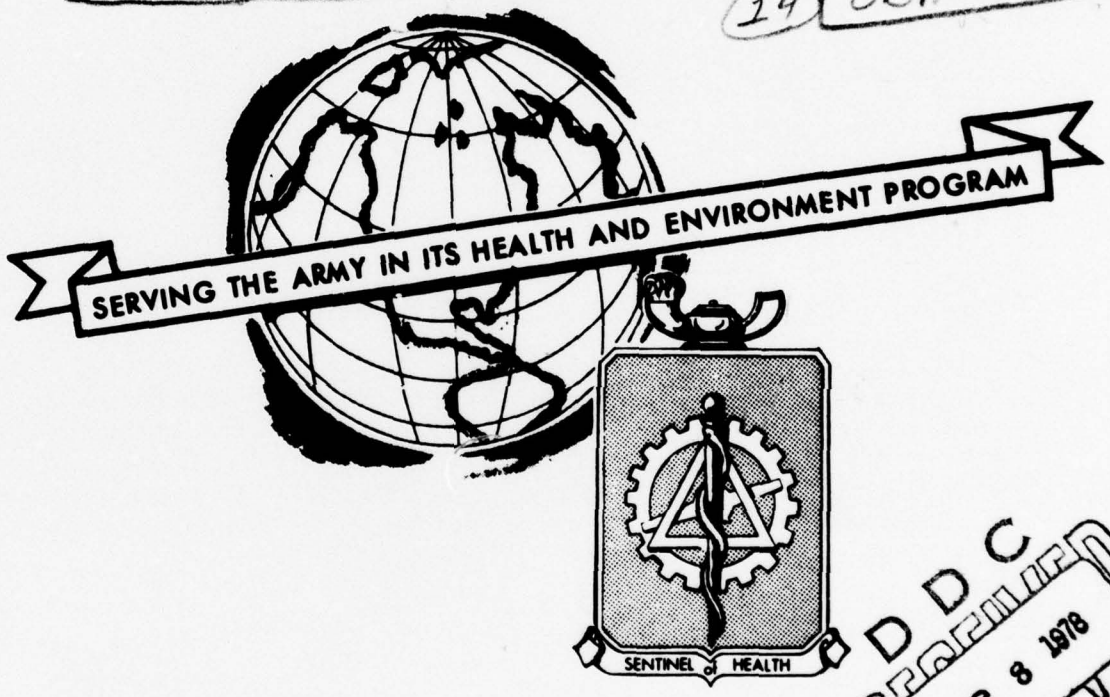

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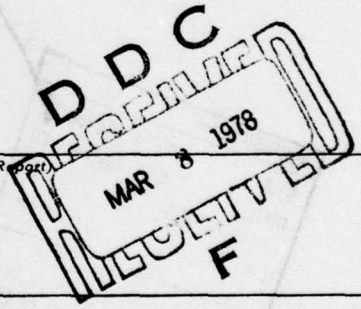

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Pesticides	Fish	Soil
Monitoring	Birds	
Environment	Residues	
Sediment	Statistical Analysis	

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

a. Results of the calendar year 1975 Department of the Army Pesticide Monitoring Program are presented. A data transformation was developed to allow statistical evaluation of the results. The data indicate that the three soil groups based on land use are significantly different. The areas having the greatest pesticide burden are the pesticide shop and storage areas. The area having the lowest pesticide burden is soil group III. The golf courses exhibit significantly higher pesticide residues than the other sites

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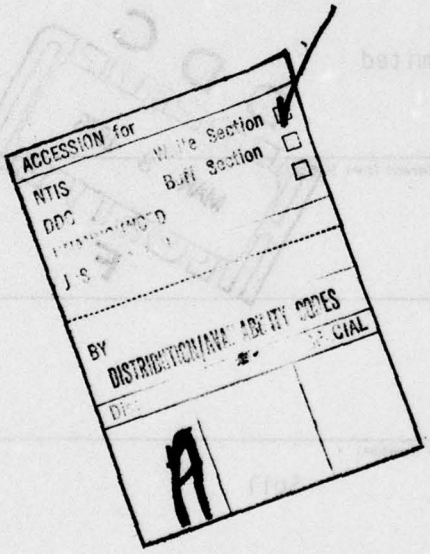
in soil group II. The four functional sediment stratifications show significantly different pesticide residues. The two functional stratifications of fish appear to be good indicators of the aquatic environment. The limited amount of bird samples places severe limitations on all conclusions from these data. The bird data do suggest that birds possess high metabolic activity. Recommendations are made with reference to sample collection and the pesticides for which analysis is done.



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Mr. Olds/jg/584-3613

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1 MAR 1978

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A summary of the pertinent findings and recommendations of the inclosed report follows.

a. Results of the calendar year 1975 Department of the Army Pesticide Monitoring Program are presented. A data transformation was developed to allow statistical evaluation of the results.

(1) The data indicate that the three soil groups based on land use are significantly different. The areas having the greatest pesticide burden are the pesticide shop and storage areas. The area naving the lowest pesticide burden is soil group III (comprised of range and training and outleased lands). Tne golf courses exhibit significantly higher pesticide residues tnan the other sites in soil group II.

(2) The four functional sediment stratifications (streams at their entrance to the installation, streams at their exit from the installation, streams originating on the installation and impounded bodies of water) show significantly different pesticide residues.

(3) The two functional stratifications of fish (top feeders and bottom feeders) yield marginally significant data. The fish appear to be good indicators of the aquatic environment.

(4) The limited amount of bird samples places severe limitations on all conclusions from these data. The bird data do suggest that birds possess nigh metabolic activity.

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b. Recommendations include:

(1) The discontinuance of sampling soil group III because of the limited amount of useful data derived.

(2) Sediment samples should only be collected from bodies of water where fish samples are available.

(3) Only bottom feeding fish should be collected as the division of top and bottom feeders is not generally productive of meaningful data.

(4) In situations where starlings are not present, the house sparrow may be substituted.

(5) Changes in the pesticides analyzed for should be made to include:

(a) The analysis of DDT on alternate years.

(b) The analysis of malathion should be excluded from sediment samples.

(c) Polychlorinated biphenyls (PCB's) should be added to the routine list.

(d) To the extent possible, pesticides in apparent widespread use throughout the Army should be added to the routine list.

FOR THE COMMANDER:

ROBERT T. WANGEMANN, Ph.D.
LTC(P), MSC
Director, Radiation and
Environmental Sciences

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PESTICIDE MONITORING ANNUAL REPORT NO. 44-0100-78
DEPARTMENT OF THE ARMY PESTICIDE MONITORING PROGRAM
EVALUATION OF ENVIRONMENTAL SAMPLES COLLECTED IN CALENDAR YEAR 1975

1. AUTHORITY.

a. AR 40-5, Health and Environment, 25 September 1974.

b. AR 200-1, Environmental Protection and Enhancement, 7 December 1973.

c. Public Law 92-516, Federal Environmental Pesticide Control Act of 1972, 21 October 1972, as amended by PL 94-140, 28 November 1975.

2. REFERENCES.

a. Entomological Special Study No. 44-004-74/75, Revised Department of the Army Pesticide Monitoring Program, 1 April 1975. National Technical Information Service, ADA 004 030, 1975, 38 pages.

b. Pesticide Monitoring Special Study No. 44-0100-77, Department of the Army Pesticide Monitoring Program, Interim Evaluation of Soil and Sediment Samples Collected in CY 1975 from Fourteen Installations, January-December 1976. National Technical Information Service, ADA 036 998, 1977, 13 pages.

3. PURPOSE. To provide the initial integrated data base for the Department of the Army Pesticide Monitoring Program (DAPMP). These environmental pesticide profiles are essential in estimating geographical and climatological effects on pesticide degradation, persistence and transport into nontarget areas. To identify specific situations requiring changes or remedial actions in pest and pesticide management practices.

4. BACKGROUND.

a. Data from previous DAPMP monitoring (prior to CY 1975) were based on incomplete sampling designs and erratic sampling. These poor data may be of complementary value but have a limited use in formal statistical evaluations.

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b. Sample collection, shipment and storage prior to extraction, cleanup and final analysis have historically presented major difficulties in assuring sample integrity in the DAPMP. Losses in sample integrity have probably precluded the reliable detection of nonpersistent pesticide residues (e.g., organophosphorus pesticide residues) and, as a result, the finding of this type of residue is highly significant. The problems with maintaining sample integrity are not completely resolved but are recognized. Techniques are being evolved to improve sample integrity.

c. The spectrum of pesticides being analyzed for versus those in current use are admittedly incongruous.

(1) This is, in part, a reflection of the state-of-the-art for multiple pesticide residue methodology.

(2) A further factor is the rapidly changing environmental concerns that receive public support.

(a) Chlordecone, 2,4,5-T and pentachlorophenol with their potential "dioxin" contaminants and the polychlorinated biphenyls (PCB's) and polybrominated biphenyls (PBB's) are now major environmental concerns that were not considered of such importance when samples were collected.

(b) New environmental concerns are additive and do not displace pesticides formerly of major importance.

(c) Additional personnel and physical resources do not keep pace with increased environmental concerns.

d. The statistical concepts employed in the sampling design are described in reference 2a. The limitations of chemical analysis and practical limitations on sample size produce a variety of "not detected" entities which must initially be entered as zero for mathematical purposes. The use of zero in most of the statistical processes introduces a bias that is unrealistic when the data are used to construct environmental pesticide profiles. The statistical techniques employed in evaluation of these data are described and explained in Appendix A. Transformed and untransformed data are used in the Tables of this report. Each Table specifies the type of data used. Statistical comparisons between populations utilizes analysis of variance techniques. To identify individual differences between the means indicated by the analysis of variance, the least significant difference (lsd) parameter is used. The lsd is a modification of the students' "t" test. Any difference between means greater than the lsd value is statistically significant at the level reported. In general, the level of significance adopted for this report is $p<0.05$. However, those differences which are highly significant ($p<0.01$) are reported as such.

e. The sample collection guidelines were modified for CY 76, owing to manpower and physical constraints, to include the collection of 12 installations on an annual basis and 11 installations on an alternate year basis for a total of 23 installations each year. These same manpower and physical constraints allowed the analysis of only 16 of these installations in CY 76 and necessitated a cut to only 12 installations to comprise the DAPMP program for CY 77 and the future.

5. RESULTS AND DISCUSSION. The installations sampled in CY 75 are listed in Appendix B. The pesticides analyzed for and the arbitrarily established detection limits appear in Appendix C. The analytical methodology is listed in Appendix D. Data for each environmental component and, where appropriate, the statistical stratifications within the component are presented and discussed before evaluating possible relationships among the components. To the extent the data lend themselves to such classifications, the influence of climate and latitude are evaluated. A single parameter has been selected for this purpose in an attempt to simplify the process. The rain and runoff soil erosivity index[1] of the universal soil loss equation is employed as the variable, assuming other components to be constant within and among these groups. Although wind erosion subsequent to application and the phenomena of spray drift during application may contribute to translocation of pesticides, these factors are difficult to evaluate retrospectively.

a. Soil. The most frequent spray target and ultimate repository for pesticides is soil. These residues are an accumulation of a variety of pesticide uses and, therefore, are an important source to use for evaluating past usage patterns. An acre, 3-inch deep, of soil has an average weight of 1 million pounds; therefore, in expressing pesticide residues in parts per million (ppm), one can conveniently use a pounds per acre equivalent when based upon a 3-inch deep sample. Thus, a 100-ppm residue in a sample can be thought of as equal to a soil loading of 100 pounds per acre or 0.0023 pounds per square foot. An overall contrast in soil data appears in Table 1.

(1) Soil Group I is comprised of land areas where pesticides are stored, mixed or disposed of, as well as landfill areas and sewage treatment/disposal areas. The practical probability of a variety of pesticide residues in these areas is high despite theoretical "recommended good practice" that would prevent such contamination.

(2) Soil Group II is comprised of those land use areas where people live, work and play. Residential and office areas, with the exception of household garden areas, generally experience a common spectrum of pests and pesticides. Recreation areas and golf courses, in particular, are usually managed with considerable pesticide use. A comparison of the golf course subset of samples with the overall Group II soil samples (Table 2) exemplifies the heavy usage on golf courses.

TABLE 1. PESTICIDE RESIDUES (PPM) DETECTED IN SOIL SAMPLES COLLECTED DURING CALENDAR YEAR 1975 (UNTRANSFORMED DATA)

Number of Samples	Group I 107			Group II* 385			Group III 205			Consolidated* 697		
Pesticide	$\bar{x}$	% Pos	Max	$\bar{x}$	% Pos	Max	$\bar{x}$	% Pos	Max	$\bar{x}$	% Pos	Max
p,p'-DDT	253.00	68	23954	0.57	52	45.60	0.08	26	4.57	39.30	47	23954
o,p'-DDT	15.10	46	842.40	0.10	27	7.84	0.01	13	1.21	2.39	26	842.40
p,p'-DDE	4.07	61	206.00	0.27	54	8.51	0.04	26	1.45	0.78	46	206.00
o,p'-DDE	0.09	4	8.96	<0.01	3	0.23	nd			0.02	2	8.96
p,p'-DDD	7.60	40	326.20	0.04	17	2.07	<0.01	5	0.25	1.18	17	326.2
o,p'-DDD	1.10	23	40.00	0.01	6	1.24	<0.01	1	0.13	0.18	7	40.00
oxychlordane	<0.01	1	0.06	<0.01	3	0.10	<0.01	1	0.03	<0.01	2	0.10
chlordane	101.00	45	4979	0.81	22	49.12	0.01	6	1.07	15.99	21	4979
trans-chlordane	0.01	8	0.42	<0.01	11	0.45	<0.01	1	0.02	0.01	8	0.45
cis-chlordane	0.02	4	1.41	0.01	4	1.36	<0.01	1	0.10	0.01	4	1.41
heptachlor epoxide	0.01	4	0.67	0.02	10	1.64	<0.01	1	0.22	0.01	6	1.64
heptachlor	<0.01	2	0.02	<0.01	1	0.25	<0.01	1	<0.01	<0.01	1	0.25
dieldrin	1.96	46	107.00	0.22	28	19.63	<0.01	3	0.06	0.42	23	107.00
aldrin	0.33	3	34.40	<0.01	1	0.89	nd			0.05	1	34.4
endrin	0.05	5	2.95	<0.01	1	0.13	nd			<0.01	1	2.95
lindane	<0.01	3	0.37	<0.01	1	0.02	nd			<0.01	1	0.37
methoxychlor	0.91	5	89.90	0.03	2	4.65	nd			0.15	2	89.90
toxaphene	0.20	1	21.50	<0.01	1	1.56	nd			0.03	1	21.50
mirex	nd			<0.01	1	0.05	nd			<0.01	1	0.05
parathion	nd			nd			<0.01	2	0.09	<0.01	1	0.09
malathion	0.04	12	0.73	nd			nd			0.01	2	0.73
diazinon	0.13	14	9.72	nd			nd			0.02	2	9.72
chlorpyrifos	0.43	10	15.01	nd			nd			0.07	2	15.01
Number of compounds	21			21			13			25		
Equivalent pounds per acre	386.05			2.10			0.15			60.68		

* αBHC at 0.02 ppm and βBHC at 0.06 ppm maximum concentration were also detected in this soil group.

TABLE 2. PESTICIDE RESIDUE DATA (PPM) FOR SOIL GROUP II CONTRACTED WITH SOILS FROM THE GOLF COURSE SUBSET OF THIS GROUP (UNTRANSFORMED DATA)

	Group II*			Golf Courses		
Number of Samples	385			88		
Pesticides	$\bar{x}$	% Pos	Max	$\bar{x}$	% Pos	Max
p,p'-DDT	0.57	52	45.6	0.41	46	15.62
o,p'-DDT	0.10	27	7.84	0.10	18	5.32
p,p'-DDE	0.27	54	8.51	0.25	47	8.51
o,p'-DDE	<0.01	3	0.23	<0.01	1	0.03
p,p'-DDD	0.04	17	2.07	0.02	12	0.56
o,p'-DDD	0.01	6	1.24	0.01	3	0.50
oxychlordane	<0.01	3	0.10	<0.01	2	0.02
chlordane	0.81	22	49.12	2.40	35	49.12
trans-chlordane	0.01	11	0.45	0.02	23	0.45
cis-chlordane	0.01	4	1.36	0.01	4	0.73
heptachlor epoxide	0.02	10	1.64	0.03	16	0.84
heptachlor	<0.01	1	0.25	nd		
dieldrin	0.22	28	19.63	0.12	32	3.14
aldrin	<0.01	1	0.89	nd		
endrin	<0.01	1	0.13	nd		
lindane	<0.01	1	0.02	nd		
methoxychlor	0.03	2	4.65	nd		
toxophene	<0.01	1	1.56	nd		
mirex	<0.01	1	0.05	nd		
parathion	nd			nd		
malathion	nd			nd		
diazinon	nd			nd		
chlorpyrifos	nd			nd		
Number of compounds	21			12		
Equivalent pounds per acre	2.1			3.36		

* Includes BHC at 0.02 ppm and BHC at 0.06 ppm maximum concentration.

(3) Data from Soil Group III are comprised of outleased lands and range and training areas. The total acreage comprising this land use classification is remarkably variable among Army installations. This variation must be taken into account in estimating specific or general environmental consequences.

(4) General soil stratifications, based on the rain and runoff soil erosivity index, are analyzed to estimate the impact of climate and topography on the use and persistence of pesticides. Climate and topography are factors, among others, that determine both directly and indirectly the kinds and abundance of pests. This determines, in part, the kinds and frequency of pesticide uses. Figure 1 is a plot of erosivity zones and scheduled monitoring installations.

(a) The total mean pesticide residues in all soils on installations are tabulated by erosivity zones in Table 3.

TABLE 3. MEAN PESTICIDE RESIDUES (PPM) IN SOILS BY EROSIVITY ZONES (Untransformed Data)

Zone	$\bar{X}$	Minimum	Maximum	(*)
Zone I	15.24	0	536.77	(chlordane)
Zone II	132.23	0	23954	(p,p'-DDT)
Zone III	8.89	0	406.33	(p,p'-DDT)
Zone IV	4.24	0	131.83	(chlordane)

* Predominant pesticide contributing to the high maximum value.

(b) The total mean pesticide residues in the three land use groups are tabulated by erosivity zones in Table 4.

(c) The total mean pesticide residues for golf courses and Soil Group II minus the golf courses are tabulated by erosivity zones in Table 5.

(5) Transformed data derived as described in Appendix A were used in a two-way analysis of variance allowing multiple factors in each cell.

Figure 1. Pesticide Monitoring Installations Classified by Erosivity Zones

	INSTALLATION	ZONE
1.	Ft Devens, MA	III
2.	West Point, NY	III
3.	Ft Dix, NJ	II
4.	Aberdeen Proving Ground, MD	II
5.	Ft George G. Meade, MD	II
6.	Ft Belvoir, VA	II
7.	Ft Eustis, VA	II
8.	Ft Bragg, NC	I
9.	Ft Jackson, SC	II
10.	Ft Gordon, GA	II
11.	Ft Stewart, GA	I
12.	Ft Benjamin Harrison, IN	III
13.	Ft Knox, KY	II
14.	Ft Campbell, KY	II
15.	Ft McPherson, GA	I
16.	Ft McClellan, AL	I
17.	Ft Benning, GA	I
18.	Ft McCoy, WI	III
19.	Ft Leonard Wood, MO	II
20.	Pine Bluff Arsenal, AR	I
21.	Ft Polk, LA	I
22.	Ft Leavenworth, KS	I
23.	Ft Riley, KS	II
24.	Ft Sill, OK	III
25.	Ft Hood, TX	II
26.	Ft Sam Houston, TX	II
27.	Rocky Mountain Arsenal, CO	IV
28.	Ft Carson, CO	IV
29.	Ft Huachuca, AZ	IV
30.	Yuma Proving Ground, AZ	IV
31.	Ft Hunter Liggett, CA	IV
32.	Ft Ord, CA	IV
33.	Presidio of San Francisco, CA	IV
34.	Ft Lewis, WA	IV

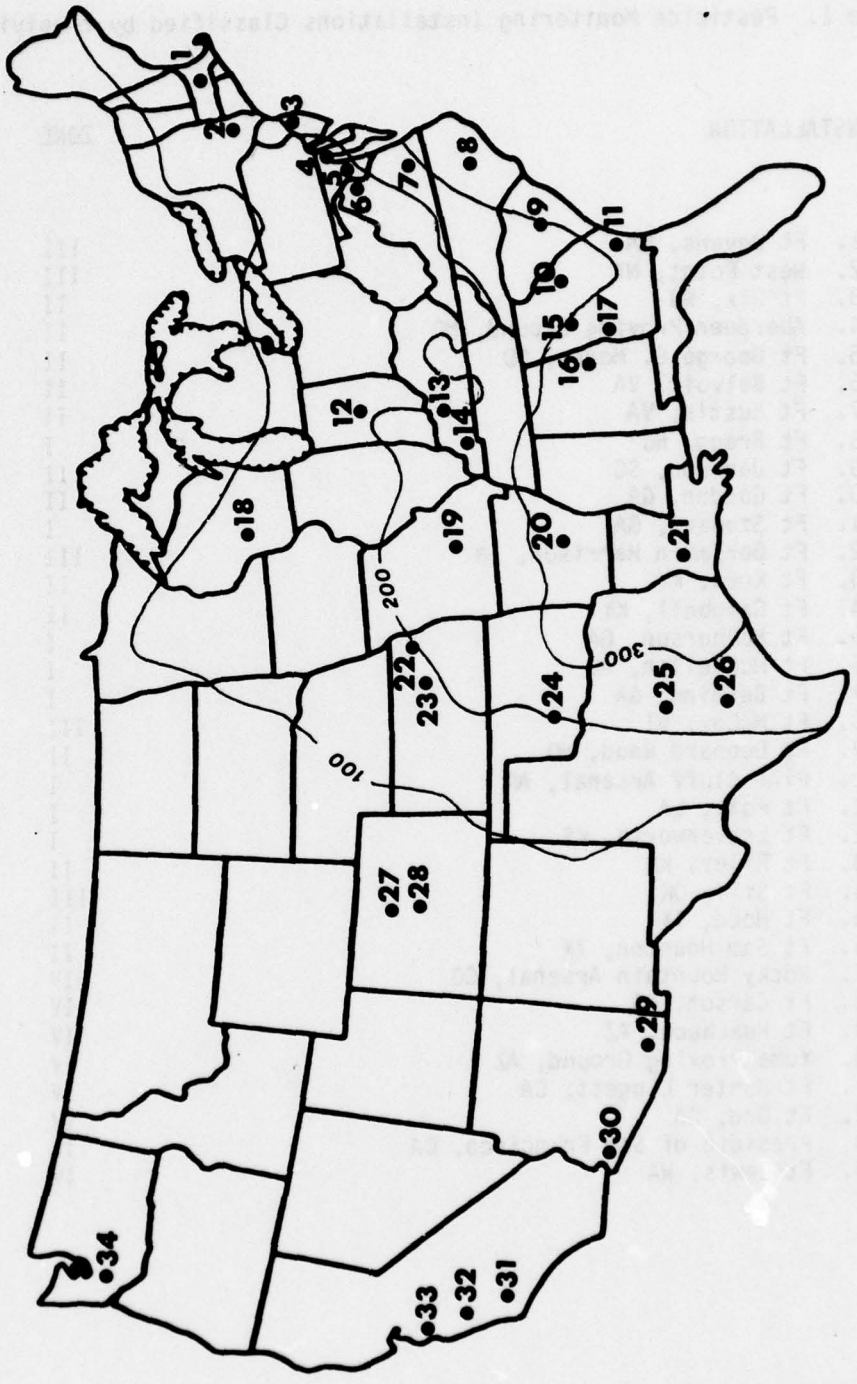
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TABLE 4. MEAN PESTICIDE RESIDUES (PPM) IN THE THREE LAND USE AREAS BY EROSIVITY ZONES (UNTRANSFORMED DATA)

	Group I			Group II			Group III		
	$\bar{x}$	Min	Max	$\bar{x}$	Min	Max	$\bar{x}$	Min	Max
Zone I	89.59	0	536.77 chlordane*	2.07	0	15.62 p,p'-DDT*	0.11	0	1.26 p,p'-DDE*
Zone II	845.49	0	23954.00 p,p'-DDT*	2.67	0	49.12 chlordane*	0.16	0	1.54 p,p'-DDT*
Zone III	50.54	0	406.33 p,p'-DDT*	1.10	0	7.85 p,p'-DDT*	0.39	0	4.57 p,p'-DDT*
Zone IV	22.65	0	131.83 chlordane*	1.78	0	25.23 chlordane*	0.006	0	0.07 chlordane* p,p'-DDT*

* Predominant pesticide(s) contributing to the maximum value.

TABLE 5. MEAN PESTICIDE RESIDUES (PPM) FOR GOLF COURSES AND LAND USE GROUP II MINUS THE GOLF COURSES (UNTRANSFORMED DATA)

	$\bar{x}$	Minimum	Maximum	Predominant Pesticide
Soil Group II (All Zones) Minus Golf Courses	1.74	0	57.73	p,p'-DDT
Golf Courses (All Zones)	3.31	0	49.12	chlordane
Zone I Golf Course	3.64	0	29.44	p,p'-DDT
Zone I, Group II Minus Golf Courses	1.54	0	27.91	chlordane
Zone II Golf Course	5.06	0	49.12	chlordane
Zone II, Group II Minus Golf Courses	1.87	0	57.73	p,p'-DDT
Zone III Golf Course	0.57	0	5.61	chlordane
Zone III, Group II Minus Golf Courses	1.2[illegible]	0	12.03	chlordane
Zone IV Golf Courses	0.65	0	4.74	dieldrin
Zone IV, Group II Minus Golf Courses	2.01	0	35.04	chlordane

(a) Soil groups based on land use were found to have a significant difference ($p<0.01$) using the transformed means for the sum of all pesticide residues (Table 6). This confirms the initial belief that stratifications based on land use permit more rapid identification of potential problem areas.

(b) The effects of golf courses on the overall pesticide residue levels in Group II soils appears in Table 7. These data show that pesticide use on golf courses is significantly greater than for other components of Group II soils.

(c) The effects of using erosivity zone classifications to estimate pesticide loss from soil to the aquatic environment via erosivity factors are analyzed in Table 8. These data indicate that only zone 4 reflects any significant difference in pesticide residues. These differences are also apparent in the untransformed data.

b. Sediment. These data are evaluated and tabulated first on the basis of four functional stratifications; i.e., flowing streams at their entrances to the installations, flowing streams at their exits, streams originating on the installation and impounded bodies of water. A second evaluation is based on erosivity zones in the same manner as pesticide residues in soils.

(1) The data based on functional stratifications are tabulated in Table 9, while those based on erosivity zones are in Table 10. A striking feature of the results is the relatively low residue levels in sediments as contrasted to the soil residue data.

(2) The total pesticide concentrations and numbers of pesticides found, when viewing the untransformed mean data strongly suggest differences among bodies of water and among erosivity zones.

(3) The number of different pesticides detected in the various stratifications indicate the diversity of contamination of this environmental component.

(4) The concentration of pesticides and the number of different pesticides detected in sediment contrast strongly with the same data from soil.

(5) The concentration of pesticides in the soil is approximately 300 times greater than the sediment (60.62 ppm versus 0.19 ppm) and the number of pesticides found in the soil is approximately twice that found in the sediment (21 versus 12). The absence of organophosphate pesticides in sediment is of particular interest.

TABLE 6. STATISTICAL COMPARISON OF TRANSFORMED PESTICIDE RESIDUE DATA (PPM) BY SOIL GROUPS

Samples	Group I 107	Group II 385	Group III 205	Group I	Group II	Group III
Minimum	0	0	0			
Mean	2.26	1.27	0.42			
Maximum	6.43	3.76	2.89			
S.D.	1.62	1.04	0.69			

s* indicates significant lsd difference
lsd 0.18†

* s indicates significant lsd difference
† indicates significance at the p<0.05 level

TABLE 7. STATISTICAL COMPARISON OF THE EFFECTS OF GOLF COURSE PESTICIDE USE ON THE PESTICIDE RESIDUES (PPM) IN SOIL GROUP II (TRANSFORMED DATA)

Samples	Group II 385	Golf Courses 88	Group II - Golf Courses 297	Golf Courses	Group II - Golf Courses
Minimum	0	0	0	s*	
Mean	1.27	1.46	1.22		lsd 0.21†
Maximum	3.76	3.69	3.76		
S.D.	1.04	1.08	1.02		

* s indicates significant lsd difference
† indicates significance at the p<0.05 level

TABLE 8. STATISTICAL COMPARISONS OF TRANSFORMED PESTICIDE RESIDUE DATA (PPM) BY EROSIVITY ZONES

Samples	Zone I 141	Zone II 291	Zone III 111	Zone IV 154	Zone I	Zone II	Zone III	Zone IV
Minimum	0	0	0	0			s*	
Mean	1.29	1.29	1.21	0.83		s*		
Maximum	4.91	6.40	4.83	4.47	s*			
S.D.	1.20	1.28	1.11	1.13			lsd 0.21†	

* s indicates significant lsd difference
† indicates significance at the p<0.05 level

TABLE 9. PESTICIDE RESIDUES (PPM) FROM VARIOUS SEDIMENT COLLECTION SITES, ALL ZONES (UNTRANSFORMED DATA)

Number of Samples	All Sites 363		Traversing/Entrance 58		Traversing/Exit 59		Originating 62		Impounded 184	
	$\bar{x}$	Max	$\bar{x}$	Max	$\bar{x}$	Max	$\bar{x}$	Max	$\bar{x}$	Max
p,p'-DDT	0.05	8.34	<0.01	0.05	<0.01	0.04	0.14	6.96	0.06	8.34
o,p'-DDT	<0.01	0.76	nd		nd		0.02	0.76	<0.01	0.20
p,p'-DDE	0.03	6.71	<0.01	0.08	<0.01	0.04	0.11	6.71	0.02	0.48
o,p'-DDE	<0.01	1.71	nd	nd	nd		0.03	1.71	<0.01	0.06
p,p'-DDD	0.23	67.08	<0.01	0.13	<0.01	0.11	1.10	67.08	0.07	4.26
o,p'-DDD	0.06	18.25	<0.01	0.03	<0.01	0.03	0.30	18.25	0.01	0.70
chlordane	0.01	1.62	0.01	0.26	0.01	0.14	<0.01	0.13	0.02	1.62
oxychlordane	<0.01	0.06	nd		nd		nd		<0.01	0.06
trans-chlordane	0.007	0.3	<0.01	0.12	<0.01	0.04	nd		<0.01	0.30
cis-chlordane	0.01	2.53	<0.01	0.05	<0.01	0.1	<0.01	0.01	0.01	2.53
dieldrin	<0.01	0.1	<0.01	0.02	<0.01	0.04	<0.01	0.05	<0.01	0.10
aldrin	<0.01	0.06	<0.01	0.02	<0.01	0.01	<0.01	0.01	<0.01	0.06
Total Concentration	0.398		0.03		0.02		1.7		0.20	
Number of Pesticides	12		9		9		10		12	

TABLE 10. PESTICIDE RESIDUES (PPM) FROM SEDIMENT SAMPLES CLASSIFIED BY ZONES (UNTRANSFORMED DATA)

Number of Samples	Zone I 86		Zone II 150		Zone III 67		Zone IV 60	
	$\bar{x}$	Max	$\bar{x}$	Max	$\bar{x}$	Max	$\bar{x}$	Max
p,p'-DDT	0.10	6.96	<0.01	0.10	0.16	8.34	<0.01	0.05
o,p'-DDT	0.01	0.76	<0.01	0.03	<0.01	0.2	nd	
p,p'-DDE	0.09	6.71	<0.01	0.17	0.03	0.48	<0.01	0.03
o,p'-DDE	0.02	1.71	<0.01	0.04	nd		nd	
p,p'-DDD	0.80	67.08	0.02	0.73	0.16	4.26	<0.01	0.11
o,p'-DDD	0.22	18.25	<0.01	0.08	0.03	0.7	<0.01	0.03
chlordane	0.01	0.77	0.02	1.62	<0.01	0.11	<0.01	0.13
oxychlordane	<0.01	0.06	nd		nd		nd	
trans-chlordane	<0.01	0.3	<0.01	0.01	<0.01	0.09	nd	
cis-chlordane	0.03	2.53	nd		<0.01	0.05	<0.01	0.01
dieldrin	<0.01	0.1	<0.01	0.02	<0.01	0.02	<0.01	0.05
aldrin	<0.01	0.03	<0.01	0.02	nd		<0.01	0.06
Total Concentration	1.29		0.05		0.39		0.01	
Number of Pesticides	12		11		9		8	

(6) Statistical evaluation of pesticides in sediments, by use of the data transformation, clearly indicates the hazards of unsophisticated data evaluations.

(a) There was a significant difference among sampling locations, using the transformed data, and these differences are listed in Table 11. These data indicate the probability of differences between streams traversing the installation and impounded bodies of water on the installation, while streams originating on the installation are not significantly different from traversing streams or impounded bodies of water.

(b) Erosivity effects (Table 12) are clearcut with zone 3 differing from all other zones, while zone 4 is generally the lowest but not significantly lower than zone 2. As an overall pattern, these data are essentially compatible with the transformed soil data.

(c) The contrasts in soil and sediment data do not indicate that erosion (and runoff) contribute in a major way to contamination of the aquatic environment.

c. Fish. Limited samples from only 24 installations provide the basis for these data. An accidential defrost incident resulted in the loss of many samples. Although feeding habits do not conform completely to such classifications, the data are evaluated on the basis of "top feeders" and "bottom feeders" in Table 13. The effects of erosivity zones are tabulated in Table 14.

(1) Utilizing the untransformed data (Tables 13 and 14), the following comparisons appear of interest.

(a) There are qualitative and quantitative differences between these two artificially designated fish populations, with the "top feeders" having an overall lower level of pesticide residues.

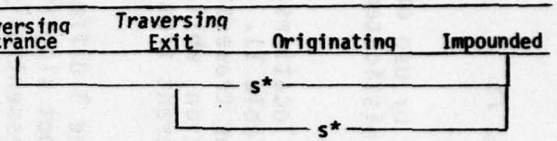
(b) Classifications by erosivity zones, based on untransformed data, indicate a greater diversity of pesticides in fish from zones 1 and 2 with the overall concentrations falling into the following order, zone 1 > 3 > 4 > 2.

(2) Statistical evaluations employing the transformed data (Table 15) do not always support instinctive conclusions arrived at from an inspection of the untransformed data.

(a) Using the least significant difference as a criterion, the "bottom feeders" do have a significantly higher pesticide residue level.

TABLE 11. STATISTICAL EVALUATION OF PESTICIDE CONTAMINATION OF SEDIMENTS COLLECTED AT VARIOUS LOCATIONS (TRANSFORMED DATA)

	All Sediment	Traversing Entrance	Traversing Exit	Originating	Impounded
No. of Samples	363	58	59	62	184
Minimum	0	0	0	0	0
Mean	0.29	0.17	0.19	0.25	0.37
maximum	4.01	1.61	1.45	4.01	3.14
S.D.	0.61	0.44	0.40	0.67	0.68

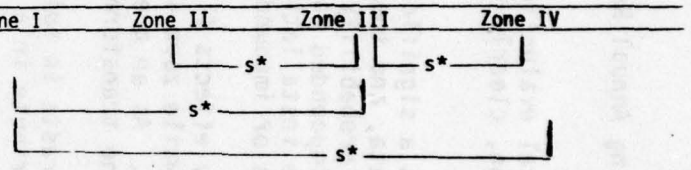


lsd = 0.15 ($p<.05$)

* s indicates significant lsd difference

TABLE 12. STATISTICAL EVALUATION OF PESTICIDE CONTAMINATION OF SEDIMENTS COLLECTED IN VARIOUS EROSIVITY ZONES (TRANSFORMED DATA)

	Zone I	Zone II	Zone III	Zone IV
No. of Samples	86	150	67	60
Minimum	0	0	0	0
Mean	0.33	0.24	0.49	0.12
Maximum	4.01	2.26	3.14	1.26
S.D.	0.72	0.51	0.79	0.33



lsd = 0.15 ($p<.05$)

* s indicates significant lsd difference

TABLE 13. PESTICIDE RESIDUES (PPM) DETECTED IN FISH SAMPLES (UNTRANSFORMED DATA)

No. of Samples	All Fish 108		Top Feeders 59		Bottom Feeders 49	
Pesticides	$\bar{x}$	Max*	$\bar{x}$	Max*	$\bar{x}$	Max*
p,p'-DDT	0.01	0.37	0.01	0.11	0.02	0.37
o,p'-DDT	<0.01	0.03	nd		<0.01	0.03
o,p'-DDE	0.19	1.99	0.16	1.46	0.22	1.99
o,p'-DDE	nd		nd		nd	
p,p'-DDD	0.15	1.95	0.10	0.74	0.21	1.95
o,p'-DDD	0.01	0.45	<0.01	0.14	0.02	0.45
methoxychlor	0.01	1.01	0.02	1.01	nd	0.64
chlordane	0.01	0.64	nd		0.02	
oxychlordane	<0.01	0.06	<0.01	0.04	0.002	0.06
trans-chlordane	0.03	0.35	0.03	0.34	0.04	0.35
cis-chlordane	<0.01	0.02	nd		<0.01	0.02
heptachlor	<0.01	0.02	<0.01	0.02	nd	
heptachlor epoxide	<0.01	0.08	<0.01	0.04	0.01	0.08
dieldrin	0.07	2.84	0.09	2.84	0.05	1.11
aldrin	<0.01	0.24	<0.01	0.24	<0.01	0.10
endrin	0.003	0.11	<0.01	0.09	<0.01	0.11
lindane	<0.01	<0.01	<0.01	0.006	nd	
toxaphene	0.02	1.52	nd		0.05	1.52
mirex	<0.01	0.17	<0.01	0.1	0.01	0.17
diazinon	<0.01	0.02	<0.01	0.02	nd	
Total Pesticides	0.52		0.44		0.66	
Number of Pesticides Detected	19		15		14	

* Minimum was below the minimum detection limit and treated as zero for statistical purposes.

TABLE 14. PESTICIDE RESIDUES (PPM) DETECTED IN FISH SAMPLES FROM VARIOUS EROSIVITY ZONES (UNTRANSFORMED DATA)

	Zone I		Zone II		Zone III		Zone IV	
Number of Samples	25		42		17		24	
Pesticides	$\bar{x}$	Max	$\bar{x}$	Max	$\bar{x}$	Max	$\bar{x}$	Max
p,p'-DDT	0.03	0.37	<0.01	0.11	0.01	0.06	<0.01	0.02
o,p'-DDT	nd		nd		<0.01	0.03	nd	
p,p'-DDE	0.31	1.99	0.17	0.84	0.18	0.57	0.10	0.76
o,p'-DDE	nd		nd		nd		nd	
p,p'-DDD	0.21	1.95	0.11	0.50	0.26	1.36	0.07	0.54
o,p'-DDD	0.03	0.45	<0.01	0.03	0.04	0.33	0.01	0.06
methoxychlor	0.04	1.01	nd		nd		nd	
chlordane	nd		0.03	0.64	nd		nd	
oxychlordane	<0.01	0.04	0.01	0.06	nd		<0.01	0.01
trans-chlordane	0.03	0.34	0.06	0.35	0.01	0.1	<0.01	0.04
cis-chlordane	nd		<0.01	0.02	nd		<0.01	0.02
heptachlor	<0.01	0.02	<0.01	<0.01	nd		nd	
heptachlor epoxide	<0.01	0.04	0.01	0.08	<0.01	0.02	nd	
dieldrin	0.03	0.38	0.03	0.48	0.02	0.1	0.23	2.84
aldrin	nd		<0.01	0.06	nd		0.02	0.24
endrin	0.01	0.11	nd		nd		0.01	0.09
lindane	nd		<0.01	0.01	nd		nd	
toxaphene	0.10	1.52	nd		nd		nd	
mirex	0.02	0.10	0.01	0.17	nd		nd	
diazinon	<0.01	0.01	<0.01	0.02	<0.01	0.02	nd	
Total Pesticides	0.81		0.43		0.53		0.44	
Number of Pesticides	13		15		9		10	

TABLE 15. COMPARISONS OF THE TRANSFORMED MEAN (PPM) PESTICIDE RESIDUE DATA FOR FISH CLASSIFIED BY VARIOUS STRATIFICATIONS

All Zones	$\bar{x}$		
Top Feeders	1.23	s*	lsd = 0.16†
Bottom feeders	1.43		

Top and Bottom Feeders Combined

Zone I	1.44	s*	
Zone II	1.43	s*	lsd = 0.22‡
Zone III	1.24		
Zone IV	1.04		

* s indicates significant lsd difference
† indicates significance at the $p<0.05$ level
‡ indicates significance at the $p<0.01$ level

(b) The order of pesticide residue levels, classified by erosivity zones, follows the order, zone 1 > 2 > 3 > 4 with significant differences between zones 2 and 4, and 1 and 4.

(c) An analysis of variance does not support conclusions that any of the previously discussed population classifications or any classifications based on site of collection, are actually different populations.

(d) The use of the least significance difference statistic is justified in support of logical and reasonable patterns.

d. Birds. A laboratory accident reduced the number of bird samples available for analysis to 13. Although this number is too small for statistical purposes, the data do have some value in that they do suggest the possible contributions from sampling this environmental component.

(1) The specific residue data for these limited samples appear in Table 16. No DDT or DDT metabolites other than p,p' DDE were detected.

(2) The data for mirex indicate that only birds collected in zones 1 and 2 contain this pesticide. Mirex, which was registered for very limited uses, would only be expected in samples which reasonably reflect the usage patterns.

(3) The data indicate rather rapid and complete pesticide metabolism in the birds, particularly oxidative metabolism, as evidenced by the absence of or the presence of very low residues of parent pesticides (e.g., p,p'-DDT, o,p'-DDT, cis and trans- chlordane). The bird data contrast the fish data where metabolism appears less rapid and complete.

e. Interactions Between Environmental Components. An initial appraisal of interactions is conveniently calculated by the use of matched data pairs; i.e., fish collected from a particular body of water/sediment from the same body, consolidated soil data from an installation/consolidated sediment data etc. to derive correlation coefficients, "r".

(1) Correlations between fish data and sediment data are tabulated in Table 17. From these data, it is apparent that a reasonable correlation exists between pesticide residues in fish and in sediment from the same bodies of water.

(a) Effects of erosivity zones are not particularly remarkable except for the rather persistent behavior of zone IV data to appear different.

(b) The data in Table 18 suggests that fish sampling may produce data more indicative of extensive contamination of the aquatic environment than the sediment.

TABLE 16. COMPARISONS OF THE UNTRANSFORMED PESTICIDE RESIDUES (PPM) IN BIRD SAMPLES

Number of Samples	All Samples 13		Zone I 4		Zone II 5		Zone III 1		Zone IV 3	
Pesticides	$\bar{x}$	Max	$\bar{x}$	Max	$\bar{x}$	Max	$\bar{x}$	Max	$\bar{x}$	Max
p,p'-DDE	0.80	3.87 (0.13)*	1.37	3.87 (0.33)	0.86	1.65 (0.53)		0.14	0.15	0.19 (0.13)
oxychlordane	0.04	0.14	0.09	0.14	0.03	0.10 (0.015)		0.02	0.01	0.01
trans-chlordane	0.01	0.06	0.01	0.02	0.01	0.06		nd	0.001	<0.01
heptachlor epoxide	0.04	0.24	0.11	0.24	0.02	0.05		0.02	nd	nd
dieldrin	0.09	0.61	0.07	0.15	0.18	0.61		0.01	<0.01	0.01
mirex	0.09	0.64	0.30	0.64 (0.09)	nd			nd		nd

* Numbers in parenthesis are the minimum levels detected.

TABLE 17. CORRELATION OF FISH TO SEDIMENT FOR IMPOUNDED BODIES OF WATER

	No. Data Pairs	r
All Fish	40	0.567*
Top Feeders	34	0.548*
Bottom Feeders	20	0.544*
All Fish, Zone I	9	0.682*
All Fish, Zone II	12	0.690*
All Fish, Zone III	9	0.801†
All Fish, Zone IV	10	0.569
Top Feeding, Zone I	6	0.831*
Top Feeding, Zone II	10	0.586
Top Feeding, Zone III	9	0.798†
Top Feeding, Zone IV	9	0.599
Bottom Feeding, Zone I	5	0.432
Bottom Feeding, Zone II	8	0.672
Bottom Feeding, Zone III and IV	insufficient data	

* indicates significance at $p<0.05$ level
† indicates significance at $p<0.01$ level
NOTE: Values without footnotes are not significant

(2) Correlations between sediment and soil pesticide residue data, based on 32 data pairs, did not indicate any significant differences.

(a) These correlations were tested employing untransformed data. It is improbable that any correlation would be apparent using transformed data.

(b) The data in Table 19 comparing all environmental components indicate that, in general, soil residues are 300 times greater than sediment residues.

(c) Data are not presently formatted so as to permit soil data from land adjacent to the sediment collections to be compared with the matching sediment data.

(3) The numbers of bird samples are inadequate to test for any correlations between an essentially nonmigratory omnivore, such as the starling, and general soil residues.

TABLE 18. COMPARISONS OF UNTRANSFORMED PESTICIDE RESIDUES BETWEEN FISH AND SEDIMENT DATA

	Sediment (363)		Fish (56)	
	Conc (ppm)	Freq (Percent)	Conc (ppm)	Freq (Percent)
p,p'-DDT	0.05	5	0.01	23
o,p'-DDT	<0.01	2	<0.01	2
p,p'DDE	0.03	14	0.17	96
o,p'-DDE	0.01	2	nd	-
p,p'-DDD	0.23	16	0.14	62
o,p'-DDD	0.06	7	0.02	18
chlordane	0.01	4	0.02	4
trans-chlordane	<0.01	2	0.03	45
cis-chlordane	0.01	1	<0.01	5
oxychlordane	<0.01	1	<0.01	12
heptachlor	nd	-	<0.01	4
heptachlor epoxide	nd	-	<0.01	20
dieldrin	<0.01	2	0.07	41
aldrin	<0.01	2	<0.01	5
endrin	nd	-	0.01	7
methoxychlor	nd	-	<0.01	2
lindane	nd	-	<0.01	2
mirex	nd	-	0.01	11
toxaphene	nd	-	0.04	4
diazinon	nd	-	<0.01	2
Total number of pesticides detected	12		19	
Total concentrations of all pesticides detected	0.42		0.53	

f. Comparisons with Published Data. Pesticide residue data in published literature are exceptionally abundant but are also generally characterized as "incomparable" for statistical purposes. Accepting the constraints of sampling plan and analytical methodology variations, it is possible to make qualitative and relative quantitative evaluations that provide some perspectives as to the characteristics of definable environments. The predominant pesticide residues are the chlorinated hydrocarbon insecticides in both the published data and in the DAPMP providing a basis for general comparisons.

TABLE 19. COMPARISONS AMONG UNTRANSFORMED DATA FOR ALL ENVIRONMENTAL COMPONENTS SAMPLED IN 1975

Number of Samples	Soil 697		Sediment 363		Fish 108		Birds 13	
	ppm	Percent	ppm	Percent	ppm	Percent	ppm	Percent
p,p'-DDT	39.36	47	0.05	5	0.01	23	nd	-
o,p'-DDT	2.39	26	<0.01	2	<0.01	2	nd	-
p,p'-DDE	0.78	47	0.03	14	0.19	96	0.80	100
o,p'-DDE	0.02	2	0.01	2	nd	-	nd	-
p,p'-DDD	1.18	17	0.23	16	0.15	62	nd	-
o,p'-DDD	0.18	7	0.06	7	0.01	18	nd	-
chlordane	15.99	21	0.01	4	0.01	4	nd	-
trans-chlordane	0.01	8	<0.01	2	0.03	45	0.01	31
cis-chlordane	0.01	3	0.01	1	<0.01	5	nd	-
oxychlordane	<0.01	2	<0.01	1	<0.01	12	0.04	77
heptachlor	<0.01	<1	nd	-	<0.01	4	nd	-
Heptachlor epoxide	0.01	6	nd	-	<0.01	20	0.04	62
dieldrin	0.42	23	<0.01	2	0.07	41	0.09	69
aldrin	0.05	<1	<0.01	2	<0.01	5	nd	-
endrin	0.01	2	nd	-	<0.01	7	nd	-
methoxychlor	0.15	2	nd	-	0.01	2	nd	-
lindane	<0.01	<1	nd	-	<0.01	2	nd	-
mirex	<0.01	<1	nd	-	0.01	11	0.09	31
toxaphene	0.03	<1	nd	-	0.02	4	nd	-
diazinon	0.02	2	nd	-	<0.01	2	nd	-
chlorpyrifos	0.07	1	nd	-	nd	-	nd	-
malathion	0.01	2	nd	-	nd	-	nd	-
parathion	<0.01	<1	nd	-	nd	-	nd	-
αBHC	<0.01	<1	nd	-	nd	-	nd	-
βBHC	<0.01	<1	nd	-	nd	-	nd	-
Total number of pesticides detected		25		12		19		6
Total concentration of all pesticides detected		60.69		0.40		0.53		1.08

(1) Soil. The pesticide residue data, on a consolidated basis from all 33 installations, can be compared with data from related land use areas in other situations.

(a) The data in Table 20 describe an environmental pesticide profile for croplands under various cropping systems for 1970.[2]

(b) The data in Table 21 describe an environmental pesticide profile for noncroplands for 1969.[3]

(c) The data in Table 22 describe an environmental pesticide profile for eight urban areas in 1969.[4]

(d) An assumption that these pesticide profiles are the result of uses associated with acceptable levels of pest management appears warranted. A further assumption that excessive pesticide use, to achieve acceptable levels of pest management, is associated with these residues cannot be rejected.

(e) These data, while reflecting past uses of exceptionally persistent pesticides, are also assumed to indicate the probable current pesticide and pest management practices.

(2) Sediment. The available data on pesticide residues in sediment cannot be summarized in tabular form for comparative purposes. The data in this report reveal essentially no correlation between soil residue data and sediment residue data.

(a) A detailed report by Barthel, et al.[5] supports this lack of correlation. "Pesticides were detected from both agricultural and non-agricultural sources; however, no evidence was found of a general buildup of chlorinated hydrocarbons in the sediments of these streams from farm use."

(b) Data from Frank, et al.[6], concerning pesticide residues in sediments in agricultural areas, do not indicate any concentrations exceeding 0.1 ppm, while from one recreational area the combined mean levels were 0.16 ppm.

(c) The relatively low pesticide residue levels in sediments are generally supported by the observations of Smith.[7] "Technical DDT applied to soil to control subterranean termites has moved very slightly in 2 decades of weathering in an open field in southern Mississippi." The data in Smith's study indicated horizontal movement of 20 inches for DDT beneath the surface. Vertical movement appears to be limited to 12 inches below the deepest area of placement.

(3) Fish. Data obtained from Henderson, et al,[8] in Table 23, indicate a considerable diversity of residue data. The systematic decrease in 1 year may be retrospectively assumed indicative of a trend particularly in view of the decreased use of DDT and most of the other persistent pesticides.

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TABLE 20.* DATA REPRODUCED FROM PESTICIDE MONITORING JOURNAL FOR COMPARATIVE PURPOSES

TABLE 8. *Chlorinated hydrocarbon residues in cropland soil by cropping region, FY-70*
(Arithmetic mean conc.)

Pesticide	Corn	Cotton	Cotton & Gen. Farming	Gen. Farming	Hay & Gen. Farming	Irrigated Land	Small Grains	Veg.	Veg. & Fruit
	Number of sites analyzed								
	713	101	117	147	184	39	105	72	42
	Arithmetic mean conc., ppm								
Aldrin	0.05	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	0.01
Chlordane	0.13	ND	0.01	0.02	0.02	0.01	<0.01	0.19	0.07
DAC	ND	ND	0.01	ND	ND	ND	ND	ND	ND
o,p'-DDE	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	ND	ND	0.01
p,p'-DDE	<0.01	0.13	0.15	0.06	0.03	0.16	<0.01	0.13	0.21
o,p'-DDT	<0.01	0.08	0.06	0.05	0.05	0.07	<0.01	0.18	0.13
p,p'-DDT	0.01	0.52	0.35	0.25	0.11	0.31	<0.01	1.06	0.69
DDTR	0.01	0.78	0.59	0.40	0.22	0.64	0.01	1.74	1.11
Dieldrin	0.07	0.04	0.02	0.01	0.01	0.05	<0.01	0.02	0.10
Endosulfan I	ND	ND	ND	ND	ND	ND	ND	ND	<0.01
Endosulfan II	ND	ND	ND	ND	<0.01	<0.01	ND	ND	<0.01
Endosulfan sulfate	ND	ND	<0.01	ND	<0.01	<0.01	ND	ND	0.01
Endrin	<0.01	<0.01	<0.01	<0.01	ND	0.01	<0.01	<0.01	0.02
Heptachlor	0.01	ND	<0.01	<0.01	<0.01	<0.01	ND	ND	<0.01
Heptachlor epoxide	0.01	ND	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Isodrin	<0.01	ND	ND	ND	<0.01	ND	ND	ND	ND
Lindane	<0.01	<0.01	<0.01	<0.01	ND	ND	ND	ND	ND
Nitralin	ND	0.02	ND	ND	ND	ND	ND	ND	ND
Ramrod	<0.01	ND	ND	ND	ND	ND	ND	ND	ND
o,p'-TDE	<0.01	<0.01	<0.01	0.01	0.01	0.02	ND	0.07	<0.01
p,p'-TDE	<0.01	0.04	0.03	0.04	0.01	0.07	<0.01	0.30	0.08
Toxaphene	ND	0.32	0.09	0.07	ND	0.68	ND	ND	0.14
Trifluralin	<0.01	0.02	<0.01	<0.01	<0.01	ND	ND	ND	ND

NOTE: ND = not detected.

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TABLE 21.* DATA REPRODUCED FROM PESTICIDE MONITORING JOURNAL FOR COMPARATIVE PURPOSES

TABLE 1.—*Pesticide residues in soil from eight cities, 1969*

City	Residues in PPM and Percent Positive Sites													
	Arsenic	o,p'-DDT	p,p'-DDT	o,p'-TDE	p,p'-TDE	o,p'-DDE	p,p'-DDE	DDTR	Dieldrin	Chlordane	Hepta-chlor	Hepta-chlor Epoxide	Toxaphene	Endrin
Bakersfield, Calif.														
Range	1.2-32.2	0.01-0.72	0.01-1.72	ND	0.01-0.33	0.01-0.16	0.01-0.92	0.02-3.08	0.01-1.98	0.07-20.48	0.02-0.10	0.05-0.18	ND	0.01-0.03
Average	7.1	0.05	0.15		0.03	0.01	0.12	0.36	0.07	0.78	<0.01	0.01		<0.01
Percent Positive sites [1]	100.0	66.0	90.0		70.0	32.0	94.0	94.0	28.0	30.0	4.0	8.0		6.0
Camden, N.J.														
Range	1.0-46.3	0.01-2.06	0.03-6.74	0.01-0.28	0.01-2.19	[2] 0.01	0.02-3.11	0.09-13.44	0.02-0.21	0.39-5.90	ND	0.02-0.39	ND	ND
Average	11.2	0.19	0.75	0.02	0.16	<0.01	0.23	1.36	<0.01	0.36		0.01		
Percent Positive sites [1]	100.0	66.0	88.0	34.0	78.0	2.0	84.0	88.0	4.0	16.0		6.0		
Houston, Tex.														
Range	0.2-15.3	0.01-3.06	0.01-3.79	[2] 0.07	0.01-0.49	0.01-0.06	0.01-0.90	0.01-7.68	0.01-1.47	0.04-12.94	0.01-0.02	0.01-0.14	[2] 0.11	[2] 0.01
Average	2.1	0.11	0.17	<0.01	0.02	<0.01	0.05	0.35	0.04	0.66	<0.01	<0.01	<0.01	<0.01
Percent Positive sites [1]	98.0	32.0	34.0	2.0	18.0	4.0	28.0	40.0	20.0	34.0	6.0	20.0	2.0	2.0
Manhattan, Kans.														
Range	0.7-72.0	0.01-1.24	0.01-4.65	[2] 0.01	0.01-0.78	0.01-0.03	0.01-1.53	0.01-8.20	0.01-0.72	0.03-<.86	0.02-0.09	0.01-0.44	[2] 12.07	ND
Average	11.5	0.11	0.45	<0.01	0.06	<0.01	0.15	0.78	0.04	0.30	<0.01	0.03	0.24	
Percent Positive sites [1]	100.0	48.0	56.0	2.0	50.0	4.0	54.0	58.0	20.0	40.0	10.0	26.0	2.0	
Miami, Fla.														
Range	0.3-33.9	0.01-5.91	0.04-42.56	0.01-0.27	0.01-5.06	0.01-0.15	0.01-11.15	0.01-52.38	0.01-8.58	0.04-16.87	0.01-0.02	0.01-0.45	14.79-52.73	ND
Average	2.3	0.79	2.67	0.02	0.41	0.01	2.09	5.98	0.72	1.59	<0.01	0.05	1.34	
Percent Positive sites [1]	80.0	86.0	94.0	24.0	84.0	8.0	100.0	100.0	64.0	64.0	6.0	50.0	4.0	
Milwaukee, Wis.[3]														
Range	1.2-54.4	0.01-1.77	0.03-15.91	0.01-0.49	0.01-1.35	0.01-0.11	0.01-2.85	0.02-22.11	0.01-1.42	0.05-10.21	0.02-0.45	0.01-0.52	ND	ND
Average	14.4	0.11	0.60	0.03	0.11	<0.01	0.21	1.07	0.04	0.45	0.02	0.04		
Percent Positive sites [1]	100.0	79.6	87.7	40.8	83.7	10.2	89.8	91.8	20.0	34.0	12.0	32.0		
Salt Lake City, Utah														
Range	1.8-74.5	0.01-1.38	0.02-2.64	0.03-0.09	0.01-0.59	0.02-0.17	0.01-0.85	0.01-5.00	0.01-1.14	0.02-7.50	0.01-0.24	0.01-0.23	ND	[2] 0.06
Average	15.7	0.09	0.23	<0.01	0.06	<0.01	0.10	0.49	0.03	0.41	0.01	0.02		<0.01
Percent Positive sites [1]	100.0	62.0	66.0	6.0	64.0	4.0	66.0	72.0	26.0	38.0	12.0	26.0		2.0
Waterbury, Conn.														
Range	0.9-37.9	0.01-1.26	0.01-6.46	0.01-0.67	0.01-1.29	0.01-0.04	0.01-2.27	0.01-10.35	0.02-0.22	0.02-8.74	0.01-0.53	0.01-0.53	ND	ND
Average	8.5	0.14	0.43	0.04	0.13	<0.01	0.19	0.98	0.01	0.96	0.01	0.02		
Percent Positive sites [1]	100.0	44.0	48.0	22.0	50.0	4.0	52.0	56.0	8.0	28.0	8.0	30.0		

NOTE: ND = not detected.

[1] Percent based on number of sites with residues greater than or equal to the sensitivity limits.

[2] One value.

[3] Based on results for 49 sampling sites.

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TABLE 22.* DATA REPRODUCED FROM PESTICIDE MONITORING JOURNAL FOR COMPARATIVE PURPOSES

TABLE 2.—*Summary of pesticide residues in noncropland soil from 11 States—FY 1969*

Compound	Number of Samples Analyzed [1]	Number of Positive Samples	Percent Positive Sites [2]	Mean Residue Level (ppm)	Range of Detected Residues (ppm)
Aldrin	199	1	0.5	<0.01	0.02
Arsenic	198	195	98.5	5.01	0.33-54.17
Chlordane	199	3	1.5	<0.01	0.04-0.50
o,p'-DDE	199	1	0.5	<0.01	0.02
p,p'-DDE	199	27	13.6	0.01	0.01-0.31
o,p'-DDT	199	7	3.5	<0.01	0.01-0.05
p,p'-DDT	199	18	9.1	0.01	0.01-0.23
DDTR	199	32	16.1	0.01	0.01-0.62
Dicofol	199	2	1.0	<0.01	0.10-0.29
Dieldrin	199	8	4.0	<0.01	0.01-0.09
Heptachlor epoxide	199	2	1.0	<0.01	0.01
p,p'-TDE	199	6	3.0	<0.01	0.01-0.18
Toxaphene	199	1	0.5	<0.01	0.52

[1] One sample per site.
[2] Percent based on number of sites with residues greater than or equal to the sensitivity limits.

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TABLE 23. MEAN DDTR* DATA (PPM) FOR FISH COLLECTED FROM SELECTED RIVER SYSTEMS

	No. of Sites	1968	1969
Atlantic Coast Streams	11	3.7	1.96
Gulf Coast Streams	4	5.7	2.98
Great Lakes Drainage	6	3.1	2.39
Mississippi River System	11	1.7	0.95
Columbia River System	6	1.6	0.80
Consolidated from Above	---	2.92	1.67

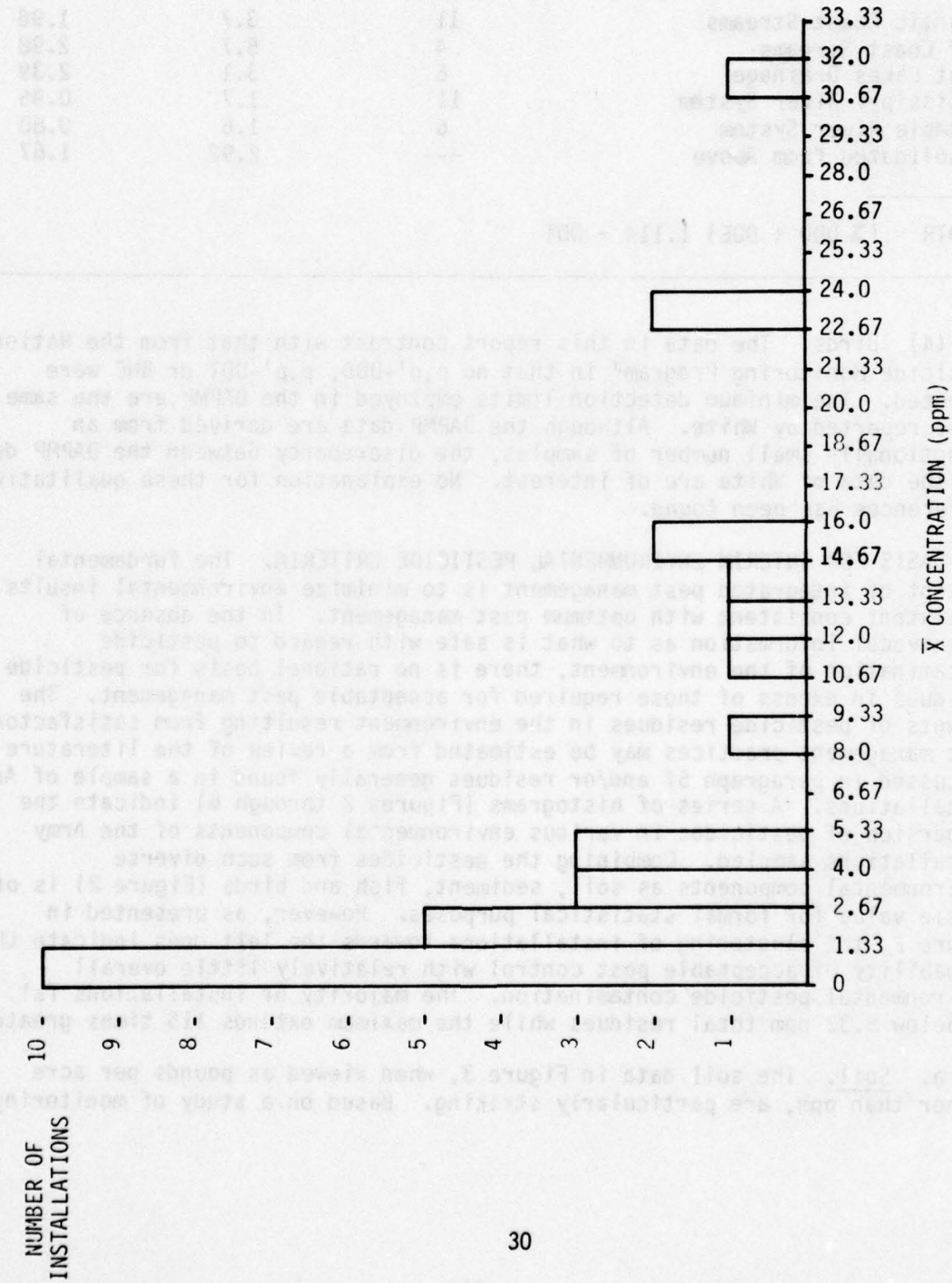
* DDTR = (Σ DDD + DDE) 1.114 + DDT

(4) Birds. The data in this report contrast with that from the National Pesticide Monitoring Program[9] in that no p,p'-DDD, p,p'-DDT or BHC were detected. The minimum detection limits employed in the DAPMP are the same as those reported by White. Although the DAPMP data are derived from an exceptionally small number of samples, the discrepancy between the DAPMP data and the data of White are of interest. No explanation for these qualitative differences has been found.

6. BASIS FOR INTERIM ENVIRONMENTAL PESTICIDE CRITERIA. The fundamental concept of integrated pest management is to minimize environmental insults to the extent consistent with optimum pest management. In the absence of unequivocal information as to what is safe with regard to pesticide contamination of the environment, there is no rational basis for pesticide residues in excess of those required for acceptable pest management. The amounts of pesticide residues in the environment resulting from satisfactory pest management practices may be estimated from a review of the literature discussed in paragraph 5f and/or residues generally found in a sample of Army installations. A series of histograms (Figures 2 through 6) indicate the dispersion of pesticides in various environmental components of the Army installations sampled. Combining the pesticides from such diverse environmental components as soil, sediment, fish and birds (Figure 2) is of little value for formal statistical purposes. However, as presented in Figure 2, the clustering of installations towards the left does indicate the probability of acceptable pest control with relatively little overall environmental pesticide contamination. The majority of installations fall at or below 5.33 ppm total residues while the maximum extends 115 times greater.

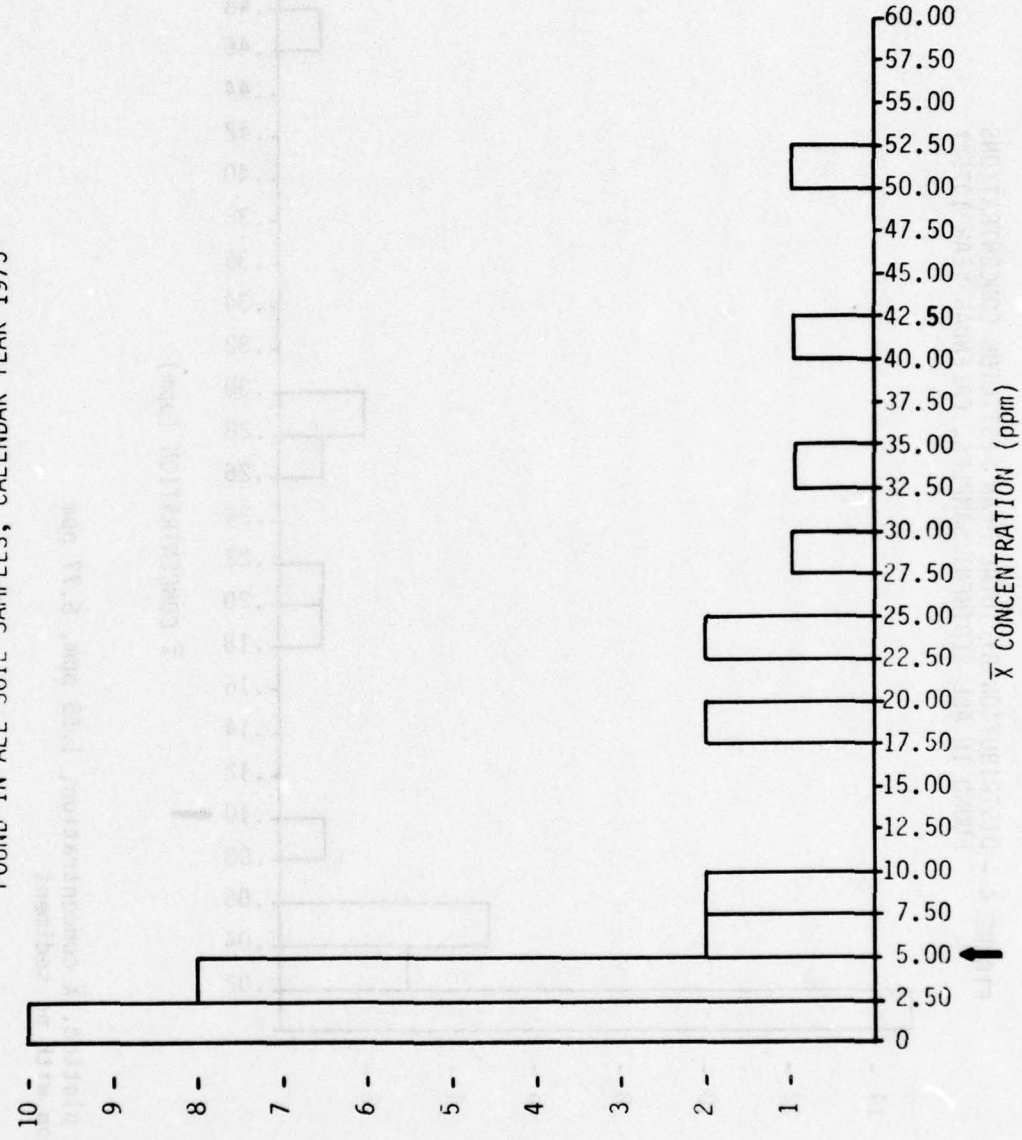
a. Soil. The soil data in Figure 3, when viewed as pounds per acre rather than ppm, are particularly striking. Based on a study of monitoring

FIGURE 2 - DISTRIBUTION BY TOTAL MEAN PESTICIDE CONCENTRATIONS FOUND IN ALL SAMPLES, CALENDAR YEAR 1975*



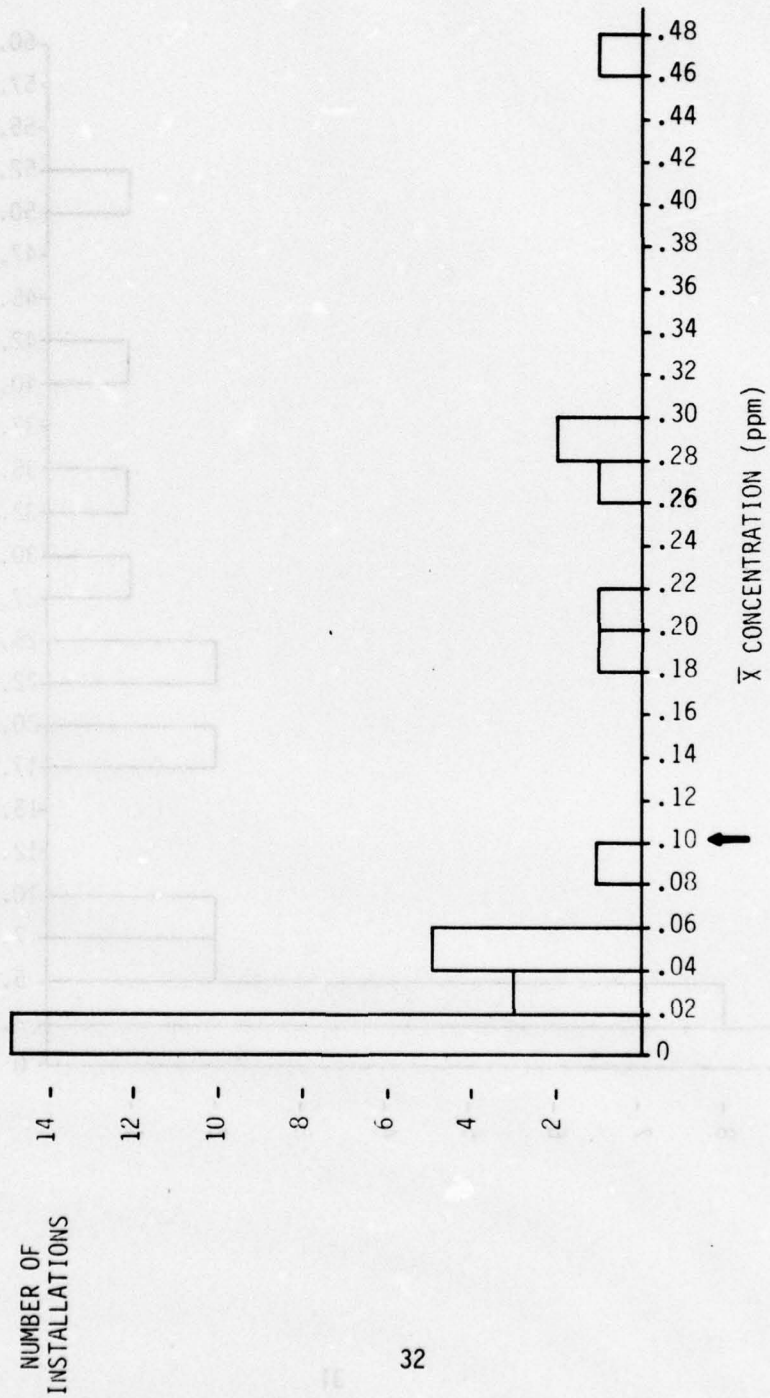
* Three installations not plotted $\bar{X}$ concentration, 53.83 ppm, 171.12 ppm, 615.34 ppm

FIGURE 3 - DISTRUBUTION BY TOTAL MEAN PESTICIDE CONCENTRATIONS FOUND IN ALL SOIL SAMPLES, CALENDAR YEAR 1975*



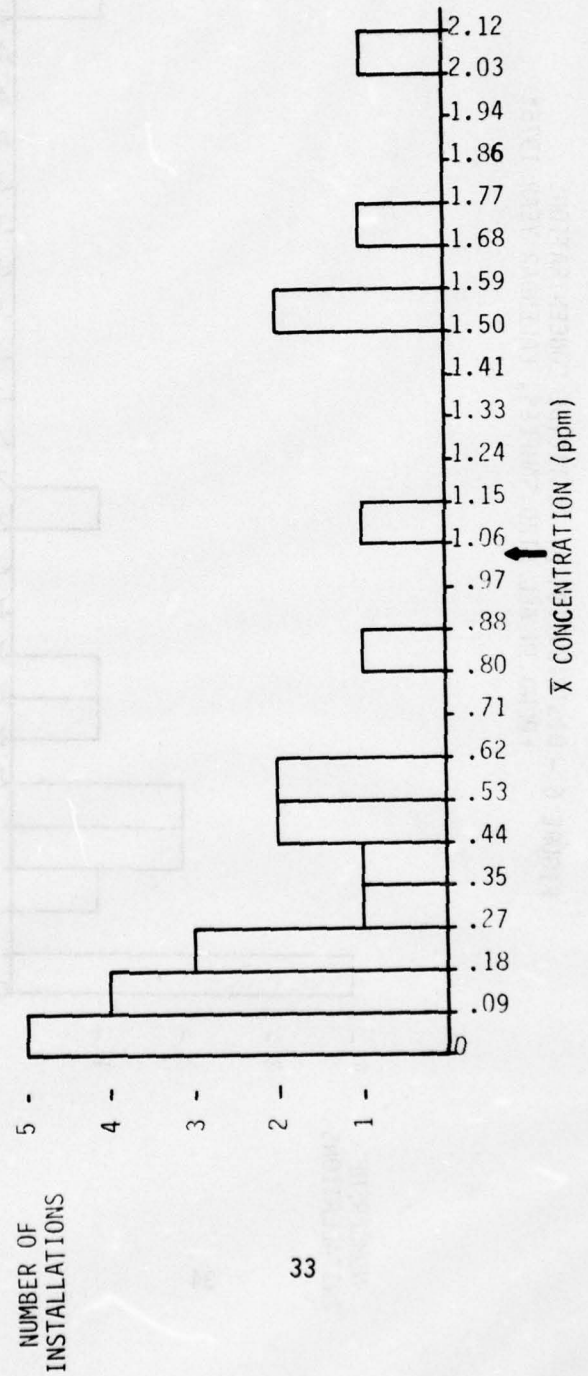
* Three values not plotted, $\bar{X}$ concentration, 90.42 ppm, 310.80 ppm, 1017.59 ppm

FIGURE 4 - DISTRIBUTION BY TOTAL MEAN PESTICIDE CONCENTRATIONS FOUND IN ALL SEDIMENT SAMPLES, CALENDAR YEAR 1975*†



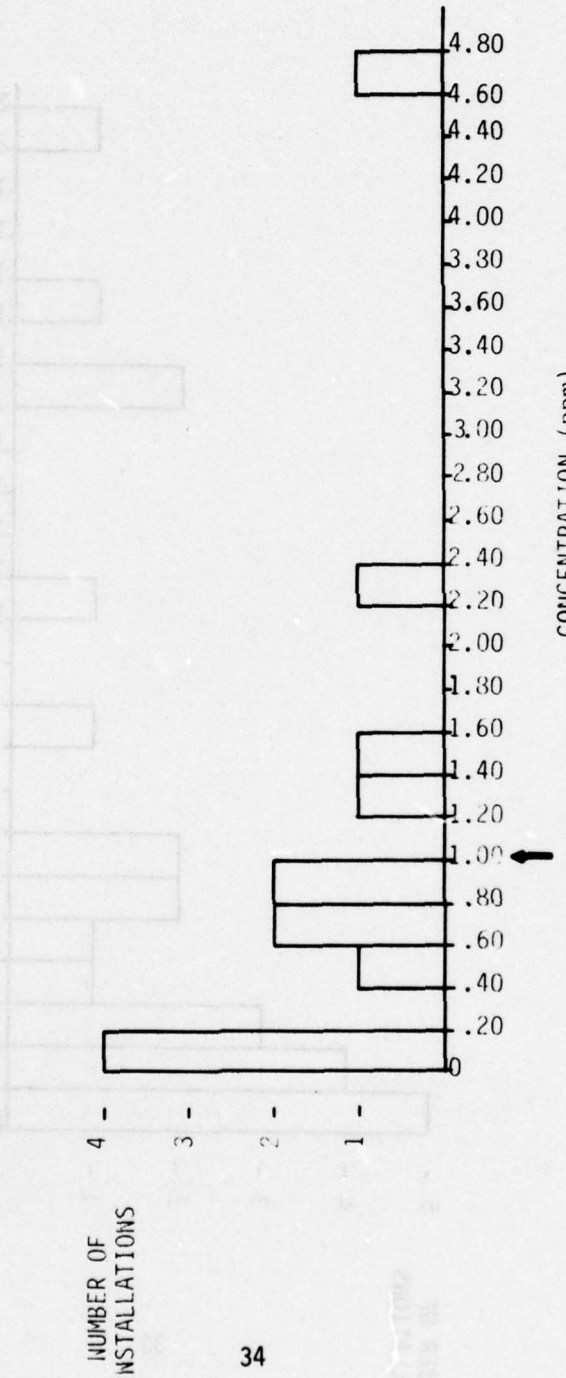
* Two values not plotted, $\bar{X}$ concentration, 1.55 ppm, 6.77 ppm
† One installation with no sediment

FIGURE 5 - DISTRIBUTION BY MEAN PESTICIDE CONCENTRATIONS FOUND IN ALL FISH SAMPLES, CALENDAR YEAR 1975*



* Samples available from only 24 installations

FIGURE 6 - DISTRIBUTION BY PESTICIDE CONCENTRATIONS FOUND IN ALL BIRD SAMPLES, CALENDAR YEAR 1975*



* Samples available from only 13 installations

literature as indicated in paragraph 5f, there is no apparent justification for soil residues in excess of 5 pounds per acre (5 ppm). This is particularly significant in that the data in Figure 3 is diluted by the inclusion of agricultural, range and training areas, etc. which are more nearly comparable with the data of Table 21 for noncroplands.

b. Sediment. The pesticide residues in sediment indicate a similar dispersion (Figure 4) to that noted with the soil data. A criteria limit of 0.1 ppm, based on the work of Frank et al.[6], and the dispersion data shown in Figure 4, certainly is not excessively low.

c. Fish. Although action levels have been established by the US Food and Drug Administration for edible portions of fish in interstate commerce, the data in paragraph 5f and the dispersions in Figure 5 support a criteria limit of 1 ppm which is not excessively low in serving as an environmental warning level.

d. Birds. The use of a criteria level of 1 ppm for all pesticide residues in starlings is based on literature discussed in paragraph 5f and the dispersions plotted in Figure 6. This Figure indicates that the majority of installations fall below this 1 ppm level. The value of 1 ppm is conservative but not exceedingly so.

e. Weighting Factors. In establishing the criteria limits presented, weighting factors were considered and given limited evaluation. However, a decision was made not to employ weighting factors for each specific pesticide.

(1) The pesticides most frequently found in high concentrations were generally the more persistent pesticides which are given the greatest weight in most weighting schemes.

(2) The majority of weighting schemes address the active ingredient and do not take into account contaminants or metabolic products.

7. CONCLUSIONS. The difficulties of evaluating pesticide distributions in an exceptionally heterogeneous environment are minimized by stratified sampling. Statistical evaluation of these data facilitate identification of situations where pesticide usage may not be consistent with the requirements of currently accepted concepts of pest management.

a. Soil Stratifications. The three land use areas do reflect patterns of pesticide application that are substantiated by statistical evaluation. Within these soil groups the following conclusions are warranted.

(1) Golf courses, with reference to the quantity of pesticides used, are significantly higher than the other sites comprising soil group II.

(2) Land use areas, described as agricultural, range, training, etc. (Soil Group III), have different environmental pesticide profiles that are statistically significant. However, the yield of useful data from Soil Group III, that serves an early warning function or contributes to understanding pesticide translocation phenomena, is the lowest value of presently available data.

(3) The sites described as pesticide shop and pesticide storage sites frequently represent such excessive pesticide contamination that statistical evaluation is redundant. These sites from Soil Group I, as well as the sewage treatment site and the landfill site, while of relatively small area, are key indicators of pesticide management practices and handling techniques. Data from this soil group should be excluded from overall general statistical evaluations in certain cases.

b. Sediment Stratifications. In general, the four sediment sampling sites represent discrete environments that should be retained. Statistical evaluation of these data support this conclusion.

c. Fish Stratifications.

(1) Although the artificial categorizations of top and bottom feeders are marginally supported by untransformed data and statistical analysis of transformed data, the yield of information from the two categorizations does not warrant further stratification.

(2) A greater diversity of pesticides and a slightly overall higher concentration of pesticides in the fish samples compared to the sediment samples indicate the value of continuing the fish sampling as an indicator of the aquatic environment.

d. Bird Samples. The limited number of samples place severe limitations on all conclusions from these data. A minimum of three separate subsamples from each installation are required to produce even minimal information. The present data set suggests that starlings possess high metabolic activity and, thus, are remarkable concentrators of DDE and certain cyclodiene pesticides and their epoxide metabolites. Mirex was detected only in birds from areas of known mirex use.

e. Interactions. Although correlations between soil and sediment pesticide residues are a reasonable expectation, none were observed. A correlation between fish and sediment pesticide residues was expected and confirmed by statistical evaluation. Insufficient data were available to test for a correlation between bird and soil residue data.

8. RECOMMENDATIONS. The number of installations comprising the DAPMP has already been reduced to a network of 12 installations. The statistical

adequacy of this sample size is in the process of being evaluated. The use of stratified sampling designs based on land use are efficient.

a. Specific Recommendations. Specific recommendations for the environmental components sampled are as follows:

(1) Soil. Soil Group III sampling should be discontinued because of the limited data available from this environment.

(2) Sediment.

(a) Sediment samples should be collected from bodies of water where fish samples are available.

(b) The stratification previously designed, subject only to the above constraint, should be continued.

(3) Fish. To the extent possible, only one classification of fish should be collected. Division into "top feeders" and "bottom feeders" are not productive of particularly meaningful information regarding general contamination of the aquatic environment.

(4) Birds. In situations where starlings are not available, the common house sparrow may be substituted even though this bird is not an omnivore.

b. Pesticides Analyzed For.

(1) In view of their persistence, DDT and metabolites should be analyzed for only every other year.

(2) The high probability that malathion would not persist but for a very short time in sediment indicates that this pesticide should be dropped from the sediment processing routine. Continued analysis for this pesticide in sediment is not justified in light of the extra analytical effort and resources required for its detection.

(3) Since polychlorinated biphenyls are of concern in environmental contamination and processing for general pesticide analysis requires cleanup procedures designed to minimize analytical interferences from these compounds, quantitative analysis for PCB's should be made a standard procedure in the DAPMP.

(4) To the extent permitted by the analytical state-of-the-art, pesticides in apparent widespread use throughout the Army should be added to the routine list.

c. Emendative Actions. Situations of excessive pesticide contamination; i.e., pesticide residues greater than those established as interim criteria in paragraph 6, must receive immediate attention to:

(1) Initiate procedural changes to eliminate or minimize further contamination.

(2) Prevent or minimize spread of contamination.

(3) Initiate procedures to accelerate biodegradation in situ.

d. Preparation of Guidelines. Generalized procedures to be followed for the items in paragraphs 8c(1), (2) and (3) should be prepared by the appropriate authority and distributed to all Army installations with active pest management programs.

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APPENDIX A
STATISTICAL ANALYSIS PROCEDURES

The statistical procedures implemented to analyze the data collected in this study require that, among other things, the variability of the data be independent of its magnitude. Upon examining the data collected it was discovered that a strong relationship existed between the mean and the variance. This suggested a violation of one of the key assumptions in the proposed analyses. A standard approach to rectify this problem is to implement a variance stabilizing transformation. A general approach to establishing such a transformation is presented by Beall [1942]*. A slight modification of the transformation suggested by Beall was

$$k^{-1/2} \sinh^{-1} [(k(100\ x + 1))^{1/2}]$$

where k is a coefficient which helps characterize the relationship between the mean and variance and x is the pesticide concentration in ppm.

Upon examining this transformation it is discovered that if (k)(x) is large the transformation approaches a log transformation. For the 1975 data it was established that a $k \approx 2.5$ which is large enough for the log transformation to be used. It was therefore decided that the following transformation would be effective in stabilizing the variability of these data.

$$\log_{10} (100\ x + 1)$$

where x is the concentration of the pesticide in ppm.

To demonstrate the effectiveness of the transformation a subset of the 1975 data was selected. In particular the p,p'-DDT soil data for the residential and cantonment areas were selected. Figure 1 shows a plot of the standard deviation (s) versus the mean ($\bar{x}$). In this plot it is noted that as the mean increases so does the standard deviation. Figure 2 shows the same plot as Figure 1 except that the data were first transformed using the log transformation shown above. In this plot very little relationship is seen between the mean and the standard deviation. Figures 3a and 3b show plots relating the concentration of the pesticide in ppm to the log transformation.

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* Beall, Geoffrey [1942]. The transformation of data from entomological field experiments so that the analysis of variance becomes applicable. Biometrika, 34, 243-262.

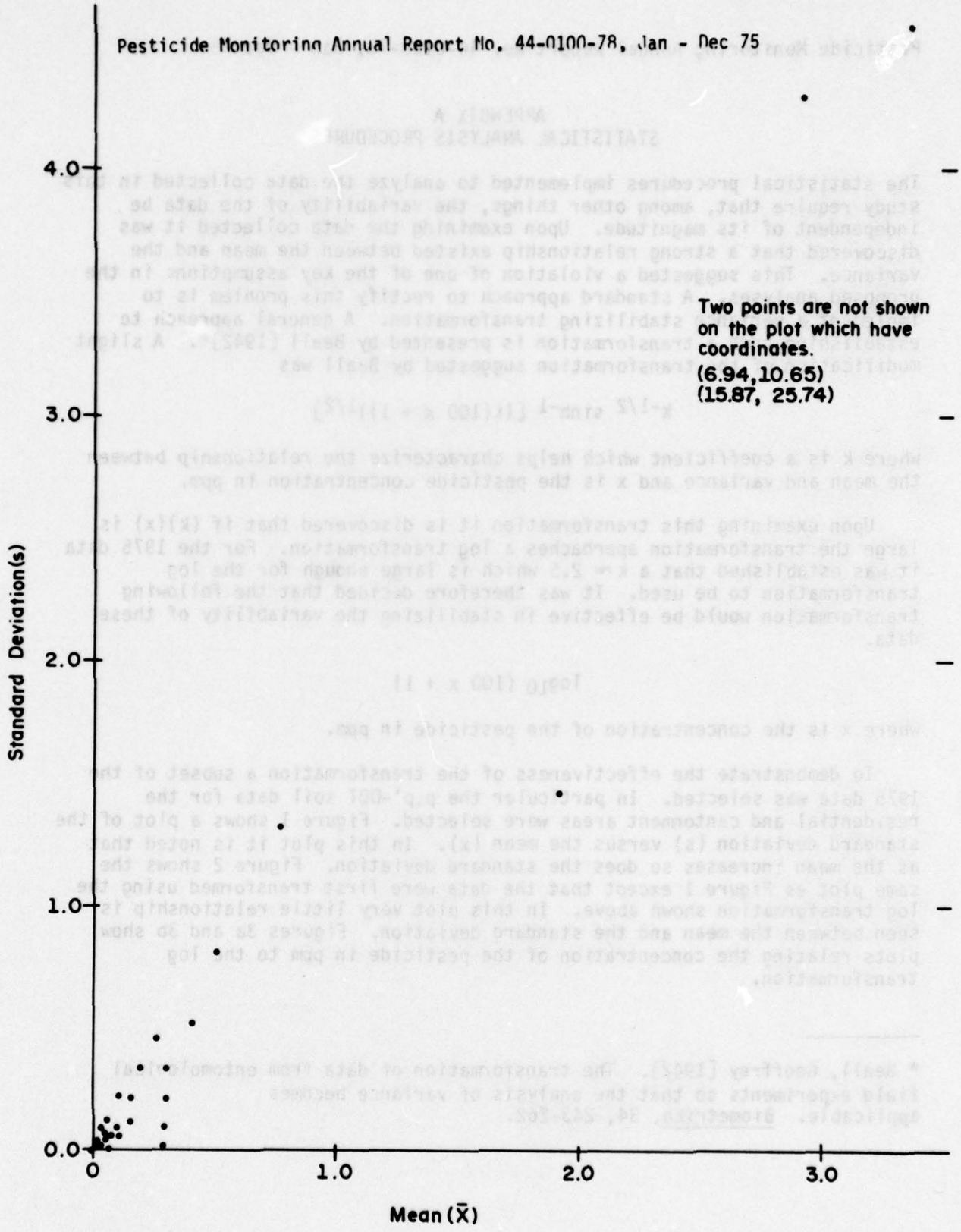

FIGURE 1: PLOT OF MEAN VERSUS STANDARD DEVIATION FOR UNTRANSFORMED DATA

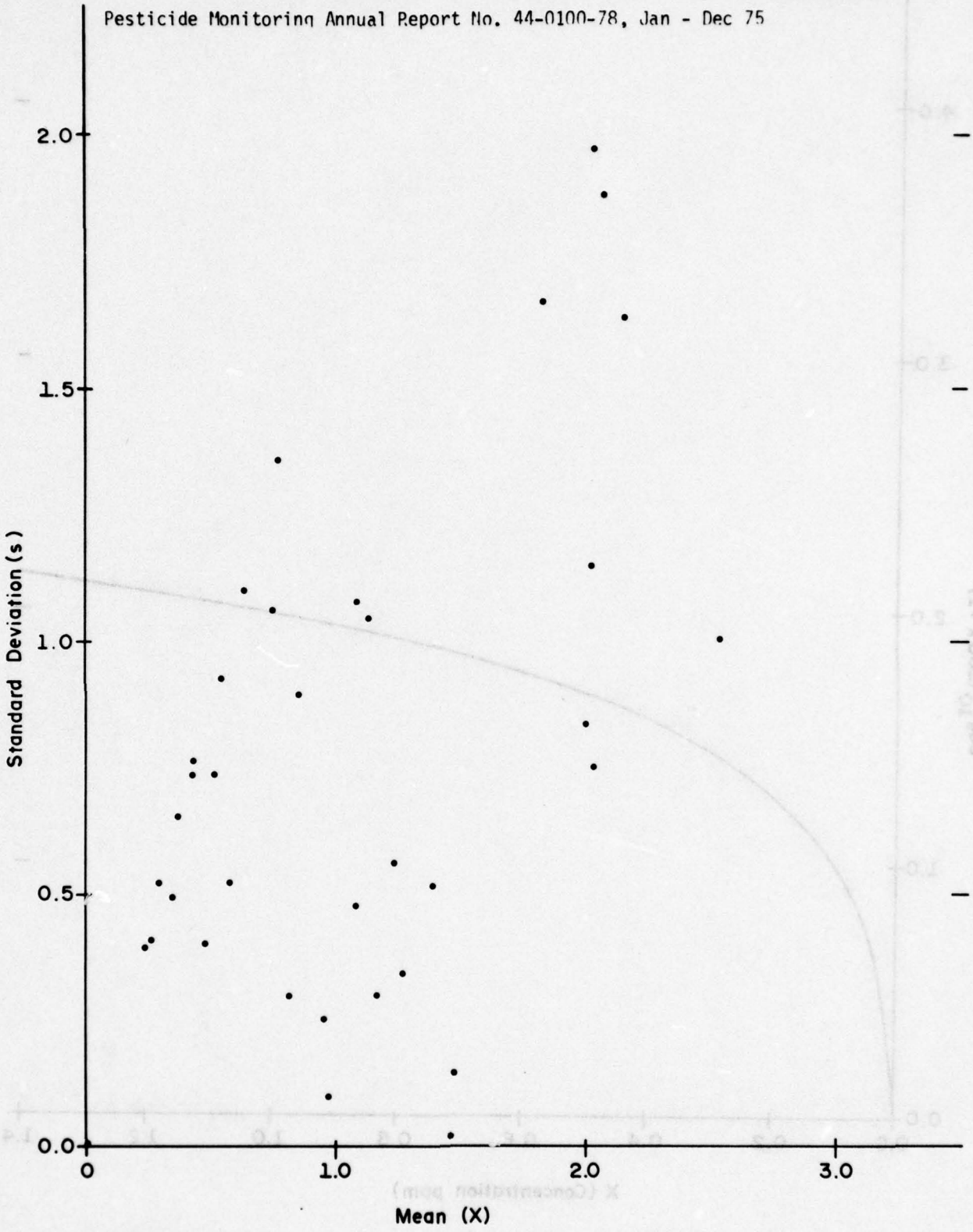

FIGURE 2: PLOT OF MEAN VERSUS STANDARD DEVIATION FOR LOG TRANSFORMED DATA

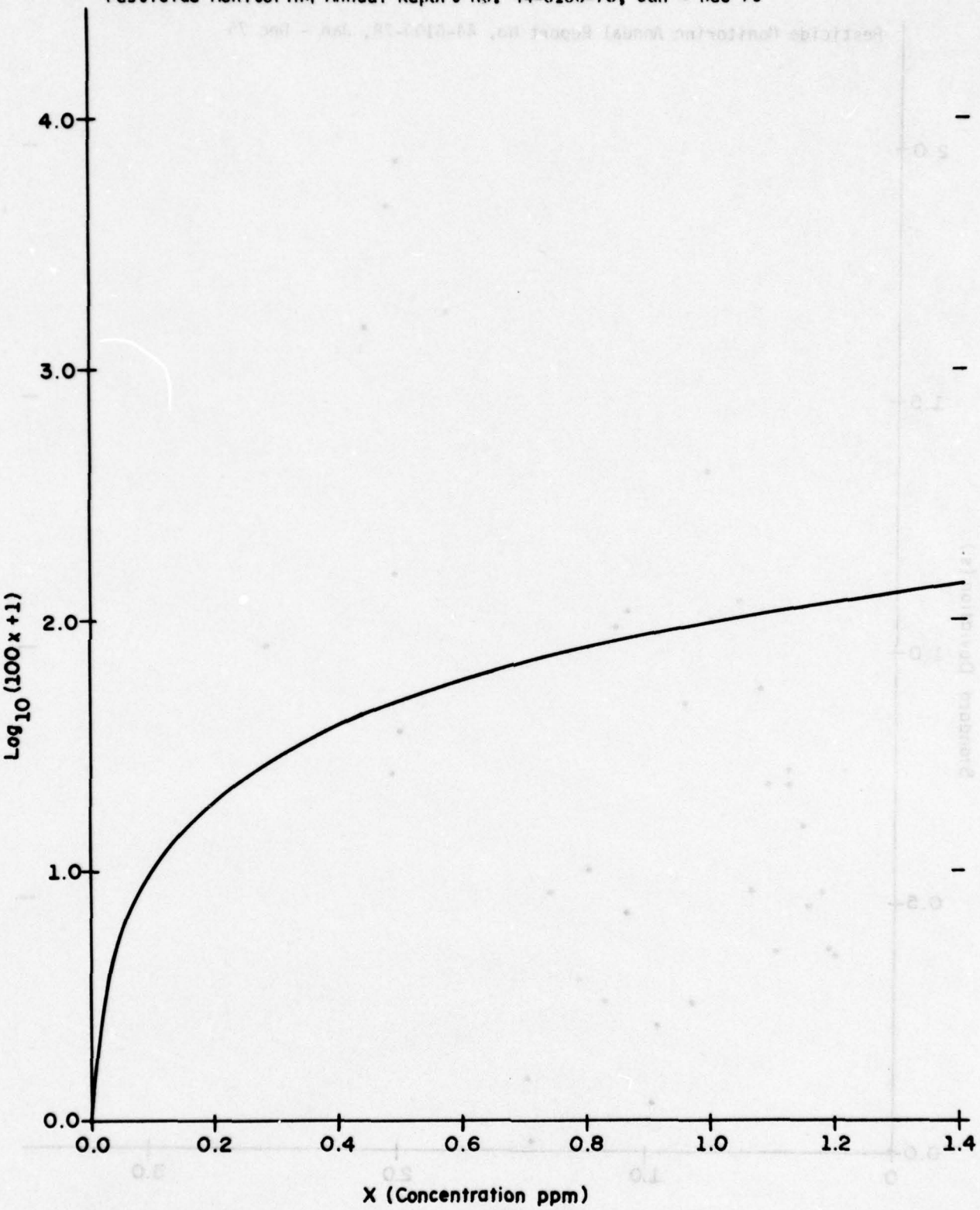

FIGURE 3a: TRANSFORMING FUNCTION FOR CONCENTRATIONS BETWEEN 0 AND 1.4 PPM

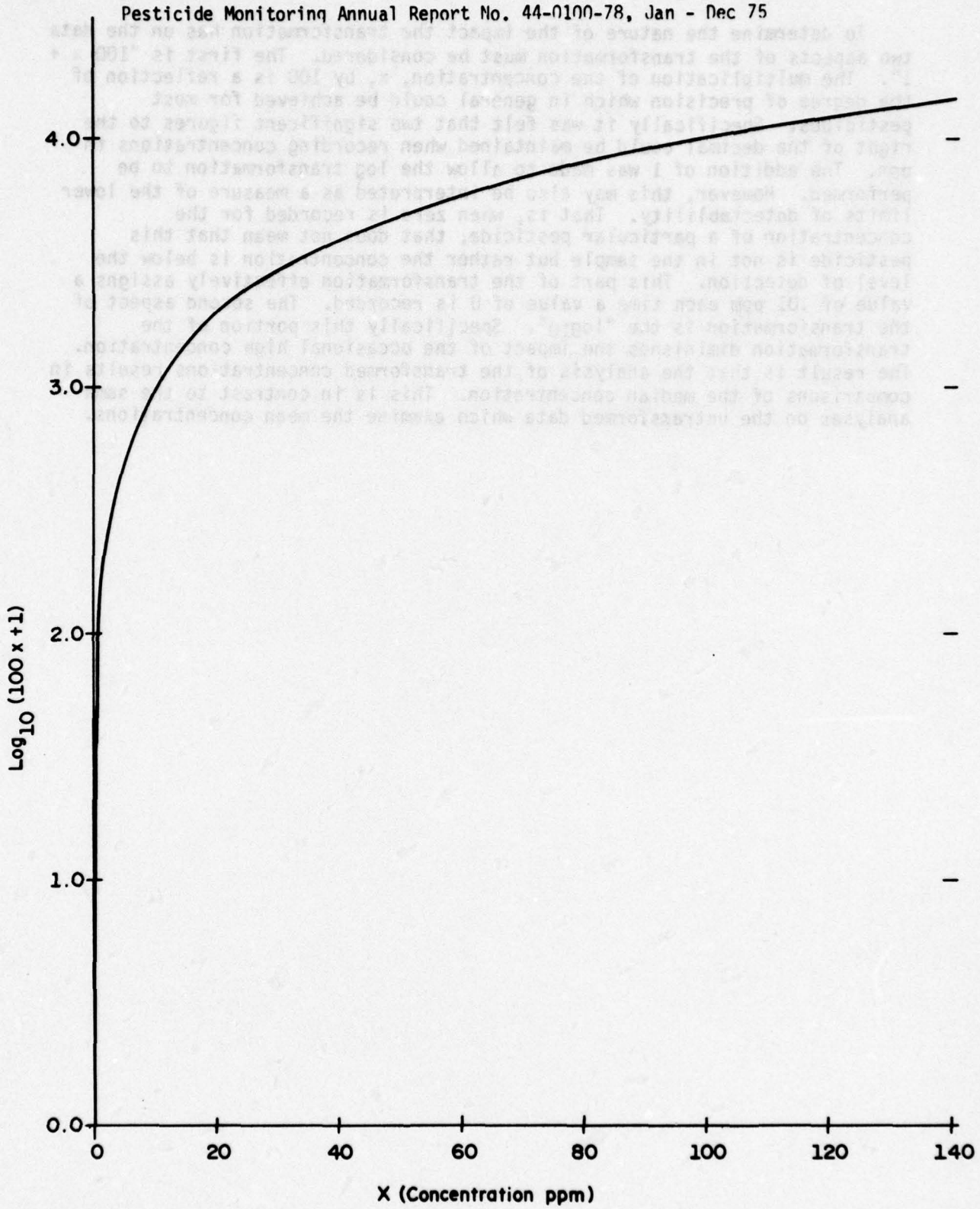

FIGURE 3b: TRANSFORMING FUNCTION FOR CONCENTRATIONS BETWEEN 0 AND 140 PPM

To determine the nature of the impact the transformation has on the data two aspects of the transformation must be considered. The first is "100 x + 1". The multiplication of the concentration, x, by 100 is a reflection of the degree of precision which in general could be achieved for most pesticides. Specifically it was felt that two significant figures to the right of the decimal could be maintained when recording concentrations in ppm. The addition of 1 was made to allow the log transformation to be performed. However, this may also be interpreted as a measure of the lower limits of detectablility. That is, when zero is recorded for the concentration of a particular pesticide, that does not mean that this pesticide is not in the sample but rather the concentration is below the level of detection. This part of the transformation effectively assigns a value of .01 ppm each time a value of 0 is recorded. The second aspect of the transformation is the "$\log_{10}$". Specifically this portion of the transformation diminishes the impact of the occasional high concentration. The result is that the analysis of the transformed concentrations results in comparisons of the median concentration. This is in contrast to the same analyses on the untransformed data which examine the mean concentrations.

APPENDIX B

INSTALLATIONS SAMPLED BY MAJOR COMMAND

FORSCOM

Fort Hunter Liggett, CA
Fort Ord, CA
Presidio of San Francisco, CA
Fort Carson, CO
Fort McPherson, GA
Fort Stewart, GA
Fort Riley, KS
Fort Campbell, KY
Fort Polk, LA
Fort George G. Meade, MD
Fort Devens, MA
Fort Bragg, NC
Fort Hood, TX
Fort Sam Houston, TX
Fort Lewis, WA
Fort McCoy, WI

TRADOC

Fort McClellan, AL
Fort Benning, GA
Fort Gordon, GA
Fort Ben Harrison, IN
Fort Leavenworth, KS
Fort Knox, KY*
Fort Leonard Wood, MO
Fort Dix, NJ
Fort Sill, OK
Fort Jackson, SC
Fort Belvoir, VA
Fort Eustis, VA

DARCOM

Yuma Proving Ground, AZ
Pine Bluff Arsenal, AR
Rocky Mountain Arsenal, CO
Aberdeen Proving Ground, MD

USACC

Fort Huachuca, AZ

Chief of Staff

West Point Military Reservation, NY

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* Sample collection was requested but no samples were received.

APPENDIX C

LISTING OF PESTICIDES/PESTICIDE METABOLITES ROUTINELY ANALYZED FOR IN CY 1975 DAPMP SAMPLES AND LOWER LIMITS OF DETECTABILITY FOR THESE PESTICIDES (PESTICIDE METABOLITES)

Pesticides/Pesticide Metabolites	Limits of Detectability (ppm)* Soil and Sediment	Fish and Birds
α-BHC	0.003	0.002
β-BHC	0.010	0.005
aldrin	0.008	0.004
chlordane (tech)	0.060	0.030
cis-chlordane	0.008	0.004
trans-chlordane	0.008	0.004
oxychlordane	0.008	0.004
o,p'-DDD	0.020	0.010
p,p'-DDD	0.016	0.008
o,p'-DDE	0.020	0.010
p,p'-DDE	0.016	0.008
o,p'-DDT	0.020	0.010
p,p'-DDT	0.030	0.015
dieldrin	0.012	0.006
endrin	0.021	0.011
heptachlor	0.003	0.002
heptachlor epoxide	0.008	0.004
lindane	0.004	0.002
methoxychlor	0.080	0.040
mirex	0.010	0.010
toxaphene	0.800	0.400
chlorpyrifos	0.012	0.004 (FPD)
diazinon	0.052	0.0032 (FPD)
malathion	0.010 (FPD)	0.005 (FPD)
methyl parathion	0.030	0.003 (FPD)
parathion	0.020	0.0035 (FPD)

* a. Limits of detectability are based on electron-capture detection, except where indicated as flame photometric detection (FPD).

b. Pesticides/pesticide metabolites not appearing on this listing are not presently being analyzed for; however, they may or may not have been present in a sample.

APPENDIX D

ANALYTICAL METHODS AND PROCEDURES USED FOR ANALYSES OF CY 1975 DA PESTICIDE MONITORING PROGRAM SAMPLES

Part 1. INTRODUCTION.

a. In this Appendix, the analytical methodology and procedures used in the preparation, extraction, clean-up, and analyses of CY 1975 DA Pesticide Monitoring Programs (DAPMP) samples are described. The analytical procedures used in the DAPMP are largely based on published procedures used by other government agencies, including the US Environmental Protection Agency (EPA), the Food and Drug Administration (FDA), the US Dept of the Interior (USDI), and the US Dept of Agriculture (USDA).

b. The analytical procedures used for the preparation, extraction and clean-up of soil and sediment samples collected under the DAPMP were adopted with certain modifications and additions from the procedure described by Stevens, et. al.[1] and Wiersma, et. al.[2]. The main modifications and additions to the above cited procedure include:

(1) The substitution of acetone for isopropanol in the extraction mixture which eliminates the need for water washings to remove the isopropanol.

(2) The extraction of 150 g soil samples instead of 300 g samples, although the 1:2 ratio of sample to extracting solvent is not modified.

(3) A Florisil column cleanup of all sample extracts is carried out prior to gas chromatographic analysis. This column cleanup procedure was added for two reasons: The use of cleaner soil extracts increases the lifespan of gas chromatographic columns and detectors, and the fractionation of pesticides among the various Florisil eluates aids in gualitative determinations.

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[1] Stevens, L. J., C. W. Collier, and D. W. Woodham, "Monitoring Pesticides in Soils From Areas of Regular, Limited and No Pesticide Use," Pestici. Monit. J, 4(3): 145-164 (1970)

. [2] Wiersma, G. B., H. Tai, and P. F. Sand, "Pesticide Residue Levels in Soils FY 1969 - National Soils Monitoring Program," Pestici. Monit. J, 6(13): 194-228 (1972)

c. The analytical procedures used for the preparation, extraction, and cleanup of fish and bird samples collected under the DAPMP are essentially identical to those described in the FDA Pesticide Analytical Manual[3] and the Official Methods of Analysis published by the Associations of Official Analytical Chemists (AOAC)[4].

d. Prior to gas chromatographic analyses, all fish and bird samples were subjected to a silicic acid columns procedure designed to separate pesticides and polychlorinated biphenyls (PCB's). The silicic acid column procedure described by Cromartie, et. al.[5] was used for separation of pesticides and PCB's in DAPMP fish and bird samples.

Part 2. STORAGE AND PREPARATION OF SAMPLES PRIOR TO EXTRACTION.

a. Soil Samples.

(1) All soil samples received under the DAPMP were received in 1-qt wide mouth glass jars fitted with Teflon® - lined lids. Upon receipt, the samples were placed in refrigerator storage at 4°C until extraction.

(2) At the time of extraction, the entire soil sample was dumped out onto a piece of aluminum foil and thoroughly mixed. After mixing, a 25 or 50 g subsample was removed for the determination of soil moisture content (Soil moisture content was determined by placing the 25 g or 50 g subsample in a foil weighing boat and allowing it to stand at room temperature for approximately 1 week. After 1 week, the subsample was reweighed and the percent moisture calculated. A 150 g subsample was then weighed into a 1-qt wide-mouth glass jar and carried through the extraction procedure described in Part 3b of this Appendix.

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[3] Pesticide Analytical Manual Volume 1, Methods Which Detect Multiple Residues, Sections 211.13f, 211.14a and 211.14d, USDHEW, FDA (Revised September, 1977).

[4] Official Methods of Analysis, Twelfth Edition, Sections 29.012(e), 29.014 and 29.015, Association of Official Analytical Chemists, Wash. D.C. (1975).

[5] Cromartie, E., W. L. Reichel, L. N. Locke, A. A. Belisle, T. E. Kaiser, T. G. Lamont, B. M. Mulhern, R. M. Prouty, and D. M. Swineford, "Residues of Organochlorine Pesticides and Polychlorinated Biphenyls and Autopsy Data for Bald Eagles, 1971-72," Pestici. Monit. J, 9(1): 11-14 (1975)

® Teflon is a registered trademark of E.I. Dupont de Nemours and Co, Inc, Wilmington, DE.

(3) The soil moisture content of most samples received for analysis ranged from 10 to 30 percent. These samples were extracted "as is" after mixing and subsampling as described above. Certain soil samples, such as those collected from desert or semi-arid regions, were obviously very dry upon receipt. In the case of these types of samples, 30 ml of hexane-extracted distilled water was mixed with the 150 g subsample prior to extraction.

(4) On occasion, a soil sample required sieving through a 1/4 inch mesh size sieve prior to mixing and subsampling in order to remove large rocks and pebbles.

b. Sediment Samples.

(1) Sediment samples were received and stored in the same manner as described above in Part 2a(1) for soil samples.

(2) At the time of extraction, the entire sediment sample was emptied into a large Buchner funnel lined with a piece of hexane-extracted filter paper and vacuum filtered until all gravitational water was removed i.e. usually 2-12 hours depending on the type of sediment. While under vacuum filtration, the contents of the Buchner funnel was protected with aluminum foil to exclude any contaminants. After removal of the gravitational water, the sediment sample was dumped from the Buchner funnel onto a piece of aluminum foil. The sample was thoroughly mixed and a 25 or 50 g subsample removed for determination of sediment moisture content. The determination of sediment moisture content was carried out in analogous manner to that previously described for soil. A 150 g subsample was then weighed into a 1-qt wide-mouth glass jar and carried through the extraction procedure described in Part 3b of this Appendix.

(3) On occasion, a sediment sample required sieving through a 1/4 inch mesh size sieve prior to mixing and subsampling to remove plant material and/or larger rocks and pebbles.

c. Fish Samples.

(1) Fish samples received under the DAPMP were received packed in dry ice in special biological shipping containers. The samples were well wrapped in aluminum foil and then placed in polyethylene bags prior to shipment. Upon receipt, the fish samples were removed as soon as possible from the dry ice containers and transferred to a freezer and stored at -10°C until processing as described in the paragraph below.

(2) After thawing, the whole fish sample was thoroughly ground or chopped (depending on the size of the fish) in a commercial food chopper. After grinding or chopping, the sample was well-mixed prior to subsampling. A subsample (50 g) was weighed into a 1-qt stainless steel blender jar and then extracted as described in Part 3c below. An additional subsample of approximately 200 g was placed in a 1-qt wide-mouth jar and stored in a freezer at -10°C until analysis of the fish sample was completed.

d. Bird Samples.

(1) Procedures for wrapping and shipment of bird samples were identical to those described above for fish samples. Upon receipt, bird samples were stored in a freezer at -10°C until processing as described in the paragraph below.

(2) After thawing and removal of feet, bills, wings and tails, the birds were skinned. Grinding, mixing and subsampling procedures for bird samples were identical to those described above for fish samples.

Part 3. EXTRACTION, CLEANUP, AND PCB SEPARATION PROCEDURES.

a. Apparatus, Reagents and Materials.

(1) Glassware.

(a) 1-qt wide-mouth jars with Teflon-lined screw caps.

(b) Erlenmeyer flasks - 500 ml, 1000 ml, 2000 ml, 4000 ml.

(c) Glass funnels - 125 mm.

(d) Chromatographic columns with Teflon stopcocks - 22 x 300 mm.

(e) Kuderna-Danish apparatus - 250 ml, 500 ml, 1000 ml flasks 10 ml concentrator tubes, 3-Ball Snyder Columns (macro)

(f) Beakers, graduated - 50 ml, 100 ml, 250 ml.

(g) Separatory funnels with Teflon stopcocks - 125 ml, 500 ml, 1000 ml, 4000 ml.

(h) Graduated cylinders - 25 ml, 50 ml, 500 ml, 1000 ml, 2000 ml.

(i) Chromatographic columns fitted with glass butted discs and with Teflon stopcocks - 22 x 400 mm.

(j) Cylindrical separatory funnels with Teflon stopcocks - 500 ml.

(k) Centrifuge jars with ground glass stopper - 500 ml.

(l) Disposable volumetric pipets - 1 ml, 5 ml, 10 ml.

(m) Disposable Pasteur pipets - 5 3/4-in and 9-in lengths.

(n) Centrifuge tubes, graduated - 15 ml, 40 ml.

(o) Culture tubes with Teflon-lined screw caps - 16 x 125 mm, 15-ml capacity.

(p) Volumetric flasks, graduated - 200 ml.

(q) Buchner funnels - 18.6 cm plate diameter.

(r) Erlenmeyer filtering flasks - 1000 ml.

(s) Wash bottles - 1000 ml.

(t) Glass beads - 3 mm diameter.

(2) Apparatus and Utensils.

(a) Waring explosion - proof blendor.

(b) 1-qt stainless steel blender cans with Teflon gaskets.

(c) Burell wrist action shaker.

(d) Eberbach variable speed shaker.

(e) Mettler balance, top loading, 1000-2000 g capacity.

(f) Sartorius balance, analytical.

(g) Blue M Laboratory Oven.

(h) Dessicator.

(i) Water bath suitable for use with Kuderna-Danish apparatus.

(j) Lab Line explosion- proof laboratory refrigerator.

(k) Kelvinator large-capacity up-right or chest-type laboratory freezer.

(l) Spatulas, stainless steel.

(m) Pipet bulbs for volumetric and Pasteur pipets.

(o) Forma-Fury Laboratory glassware washer.

(p) USA Standard Testing Sieve, 1/4-in mesh size.

(3) Reagents, Solvents and Other Supplies.

(a) Hexane - pesticide quality.

(b) Petroleum ether - pesticide quality.

(c) Ethyl ether - pesticide quality.

(d) Ethyl alcohol - absolute.

(e) Acetonitrile - pesticide quality.

(f) Methylene chloride - pesticide quality.

(g) Isooctane - pesticide quality.

(h) Acetone - pesticide quality.

(i) Sodium sulfate - anhydrous, granular, hexane washed.

(j) Sodium chloride - hexane washed.

(k) Distilled water - hexane washed.

(l) Whatman no. 43 filter paper - 18.5 cm, hexane extracted.

(m) Glass wool - silanized - hexane washed.

(n) Florisil® - PR grade (60-100 mesh) purchased activated at 1250°F and stored in dark in glass containers with foil line caps. Activated overnight at 130°C in chromatographic columns prior to use.

(o) SilicAR® CC-4 special for column chromatography - purchased in dark glass bottles and stored in the dark. Before use, SilicAR was placed in enamel pans covered with aluminum foil and heated in an oven at 130°C for 24 hours or longer. The SilicAR was deactivated by first weighing 100 g into a 500 ml glass centrifuge bottle. The bottle was then sealed and allowed to cool to room temperature in a desiccator. Once at room temperature, 3 ml of water was added. The centrifuge bottle was then tightly stoppered and shaken on a wrist action shaker for a period of 4 hours. The centrifuge bottle was then returned to the desiccator and allowed to equilibrate for 15 hours. Desired activity was retained for about 5 days if stored in a desiccator.

b. Soil and Sediment Samples.

(1) Extraction.

(a) After preparing, as described above in Part 2 a and b of this Appendix, 150 g subsamples of soil or sediment were extracted with 300 ml of 3:1 -hexane:acetone for 2 hours on a variable speed mechanical shaker. After shaking, the samples were allowed to stand for 1 hour to allow settling of particulate matter.

(b) Using a graduated cylinder, 100 ml aliquots of the sample extracts were measured. The aliquots were then passed through chromatographic columns containing approximately 6 inches of sodium sulfate. Following elution of the sample extracts, the columns were rinsed with 25-30 ml of hexane. The extracts and rinses were collected in 250 ml Kuderna-Danish apparatus. The extracts were concentrated in a water bath to 10 ml. The extracts were transferred to 15 ml screw-cap culture tubes with Teflon cap liners and placed in a freezer until cleanup.

® Florisil is a registered trademark of Floridin, Company, P.O. Box 989, Tallahassee, FL.

® SilicAR is a registered trademark of Mallinckrodt Chemical Works, P.O. Box 5439, St L.

(2) Cleanup.

(a) Florisil columns were prepared as follows: To a chromatographic column (22 mm x 300 mm) containing a glass wool plug was added 40 ml (measured in a small tared beaker) of Florisil - pesticide grade (60/100 mesh). After settling of the Florisil by gentle tapping, the column was topped with a one-half-inch layer of sodium sulfate. The Florisil column was activated by placing it in an oven at 80° - 100°C for a minimum of 16 hours.

(b) Florisil columns, prepared and activated as described above, were allowed to cool and then were pre-wet with 40-50 ml of hexane. Sample extracts from extraction step (1)(b) above were further concentrated to 2-3 ml under a nitrogen stream and carefully transferred using Pasteur pipets onto the Florisil columns.

(c) Graduated Erlenmeyer beakers (250 ml) were placed under the columns and the columns were eluted with 200 ml of 6 percent ethyl ether/petroleum ether mixture. The beakers were changed and the columns eluted next with 200 ml of 15 percent ethyl ether/petroleum ether mixture. The beakers were again changed and the columns eluted finally with 200 ml of 50 percent ethyl ether/petroleum ether mixture. The elution rate for each of the three fractions was maintained at approximately 5 ml/min. NOTE: Ethyl ether should be free of peroxides and must contain 2 percent v/v of absolute ethanol.

(d) The beakers containing the 6 percent, 15 percent and 50 percent eluate fractions were tared to exactly 200 ml with additional petroleum ether and mixed with a Pasteur pipet. Aliquots (10 ml for the 6 percent and 15 percent soil fractions, 20 ml for the 6 percent and 15 percent sediment fractions, 12 ml for the 50 percent soil fractions, and 20 ml for the 50 percent sediment fractions) were transferred to appropriate 15 ml or 40 ml graduated centrifuge tubes and concentrated to obtain appropriate definitive volumns for gas chromatographic analysis. Routine definitive volumes used were 160 ml for the 6 percent and 15 percent soil fractions, 100 ml for the 6 percent and 15 percent sediment fractions, 16.7 ml for the 50 percent soil fraction, and 10 ml for the 50 percent sediment fraction (based on 200 ml total volume for each fraction).

(e) After appropriate concentration, the 6 percent, 15 percent, and 50 percent extract fractions were transferred to 15 ml screw cap culture tubes and stored in a freezer until gas chromatographic analysis.

c. Fish and Bird Samples.

(1) Extraction.

(a) To 1-qt stainless steel blender jars containing 50 g fish or bird subsamples prepared, as described in Part 2c and d of this Appendix, was added an amount of sodium sulfate equivalent to twice the weight of the subsample, i.e., 50 g subsample + 100 g sodium sulfate.

(b) Samples were then extracted using a high speed blender with successive 150-ml, 100-ml, and 100-ml portions of petroleum ether. After each extraction, the supernatant petroleum ether was filtered by gravity through glass funnels lined with preextracted filter paper into 1000-ml round bottom flasks. After the petroleum ether extractions, the residues from the blender jars were transferred to the glass funnels and the jars and residue were rinsed with several small portions of petroleum ether. The rinses were combined with the petroleum ether extracts in the 1000-ml round bottom flasks.

(c) The combined petroleum ether extracts and rinses were passed through chromatographic colums (22x300 mm) containing 6 to 8 inches of anhydrous sodium sulfate. The flasks and columns were rinsed with a small portion of hexane. Extracts and rinses were collected in 1000-ml Kuderna-Danish apparatus.

(d) The sample extracts were concentrated on a water bath to 10 ml. After concentration, the extracts were transferred to previously weighed 50-ml Erlenmeyer beakers, and evaporated under a gentle nitrogen stream until all solvent was removed. The resulting fat material was weighed (resulting fat weights for most fish and bird samples ranged from 0.5 to 3.0 g) and then transferred using Pasteur pipets and small measured amounts of petroleum ether carrier solvent into 125-ml separatory funnels. Additional petroleum ether was added to the separatory funnels so that the total volumes of fat and petroleum ether were 15 ml.

(e) The petroleum ether-fat extract solutions were extracted successively with four 30-ml portions of acetonitrile saturated with petroleum ether. The separatory funnels were shaken vigorously for 1 minute during each extraction. Following each extraction, the acetonitrile layers were drained into 1000-ml separatory funnels containing 650 ml of water, 40 ml of saturated sodium chloride solution and 100 ml of petroleum ether.

(f) The 1000-ml separatory funnels containing the combined extracts from the four acetonitrile extractions were shaken moderately for 30 to 40 seconds. Following separation of the layers, the aqueous layers were drained into second 1000-ml separatory funnels. Petroleum ether (100 ml) was added to the second separatory funnels and the funnels were shaken vigorously for 15 to 30 seconds. The layers were allowed to separate and then the aqueous layers were discarded. The petroleum ether layers in the second separatory funnels were combined with the petroleum ether layers in the original separatory funnels, and the combined petroleum ether layers were washed with two successive 100-ml portions of water. The aqueous layers were discarded between washings.

(g) The petroleum ether extracts from step (f) above were passed through chromatographic columns containing 6 to 8 inches of sodium sulfate. The separatory funnels and columns were rinsed with three 10-ml portions of petroleum ether. The extracts and rinses were collected in 500-ml Kuderna-Danish apparatus. The extracts were concentrated to 10 ml, transferred to 15-ml screw-cap culture tubes, and stored in a freezer until cleanup.

(2) Cleanup. The sample extracts from extraction step (1)(g) above were further concentrated under nitrogen to 2-3 ml, and then transferred to Florisil columns. The procedure used for Florisil column cleanup of fish and bird samples was identical to that previously described for soil and sediment samples except the 6 percent, 15 percent and 50 percent eluate fractions were each collected in 500 ml Kuderna-Danish apparatus and then concentrated to 10 ml. The 6 percent eluates were transferred to 15 ml screw-cap culture tubes and stored in a freezer until processing through the silicic acid column PCB separation procedure described Part 3c(3) below. The 15 percent and 50 percent eluates were transferred to 15 ml screw-cap culture tubes and stored in a freezer until gas chromatographic analysis. At the time of analysis, after screening for routine organophosphorous pesticides, the 15 percent eluate fractions were diluted 1:10 to obtain appropriate 100 ml definitive volumes for analysis of routine organochlorine pesticides.

(3) PCB Separation Procedure.

(a) The 6 percent eluates from the Florisil column cleanup procedure were processed directly without preliminary gas chromatographic screening, through the silicic acid column PCB separation procedure.

(b) Silicic acid columns were prepared as follows: silicic acid (20 g), deactivated as described in Part 3a(3) was weighed into a 250-ml Erlenmeyer beaker and immediately slurried with 80 ml of petroleum ether. The slurry was quickly poured through a long-necked glass funnel onto a chromatographic column (22x400 mm) with stopcock open. The glass funnel and the sides of the column were washed down with additional small portions of petroleum ether.

While gently tapping the column with a wooden ruler, the petroleum ether was allowed to drain through the column until the level of petroleum ether was about 3 mm above the surface of the silicic acid. The column stopcock was then closed.

(c) The 6 percent eluate fractions from cleanup step c(2) above were further concentrated to about 2-3 ml under a nitrogen stream. NOTE: Six percent eluate fractions from fish and bird samples which contained more than >2.0 g fat material (as determined in extraction step c(1)(d) above were cut by one-half prior to concentrations to 2-3 ml in order to prevent overloading of the silicic acid column. A 100 ml graduated cylinder was placed under the silicic acid columns. The concentrated 6 percent eluate fractions were then slowly and carefully pipetted onto the columns using long-stemmed Pasteur pipets. The column stopcocks were opened and the solvent level drained to 3 mm. Three additional 2-ml rinse aliquots of petroleum ether were pipetted onto the columns slowly washing down the sides of the columns. After the addition of each 2 ml petroleum ether aliquot the solvent level was drained to 3 mm. The column stopcocks were then closed and an additional 10 ml of petroleum ether pipetted onto the columns. A cylindrical separatory funnel containing 400 ml of petroleum ether was placed on the top of each column; the stopcocks were opened and petroleum ether elutions (at the rate of approximately 5 ml/min) were commenced. Elutions were continued until exactly 100 ml of petroleum ether eluate was collected in the 100 ml graduated cylinders. Then, without closing the column stopcocks, the 100 ml graduated cylinders were removed and 500 ml graduated cylinders immediately placed under the columns. Elutions were continued until exactly 300 ml of petroleum ether eluate was collected in the 500 ml graduated cylinders, after which the column stopcocks were closed. The 100 ml and 300 ml petroleum ether eluates comprised silicic acid column fractions I and II respectively. Two hundred milliliters of a 1:19:80 acetonitrile: n-hexane: methylene chloride mixture was added to the cylindrical separatory funnels. A 250 ml graduated cylinder was placed under the columns, the stopcocks were opened and elutions of above solvent mixture (5 ml/min) were commenced. The columns were allowed to elute to dryness. The resulting mixed solvent eluates comprised silicic acid column fraction III.

(d) Silicic acid column fractions I, II and III were transferred to appropriate sized 250 ml or 500 ml Kuderna-Danish apparatus and concentrated to 10 ml. The concentrated I, II and III fractions were transferred to 15 ml screw cap culture tubes and stored in a freezer until gas chromatographic analysis. At the time of gas chromatographic analysis, silicic acid column fractions I, II and III, were diluted 1:10 to obtain appropriate definitive volumes i.e., 100 ml for analysis of routine organochlorine pesticides. Fraction III was also screened at the 10 ml definitive volume for routine organophorphorous pesticides.

Part 4. GAS CHROMATOGRAPHIC ANALYSIS PROCEDURES.

a. Preparation of Analytical Standards.

(1) Sources of Analytical Standards.

(a) EPA, Quality Assurance Section, Environmental Toxicology Division, Health Effects Research Laboratory, Research Triangle Park (RTP), NC 27711.

(b) EPA, Pesticides Reference Standards Section, Chemistry Branch, Registration Division, Washington, DC 20460.

(c) Poly Science Corporation, 6366 Gross Point Road, Miles, Illinois 60648.

(d) Pesticide Manufactures.

(2) Apparatus, Materials and Reagents.

(a) Mettler M5 Analytical Balance.

(b) Foil Weighing Boats.

(c) Glass Weighing Boats.

(d) Class A volumetric flasks - 100 ml, 200 ml.

(e) Class A volumetric pipetts - 1 ml, 2 ml, 3 ml, 4 ml, 5 ml, 6 ml, 7 ml, 8 ml, 9 ml, 10 ml.

(f) Benzene - pesticide grade.

(g) Isooctane - pesticide grade.

(h) Disposable Pasteur pipets - 9 in.

(i) Pipet bulbs for volumetric and Pasteur pipets.

(j) Small stainless steel spatulas.

(k) Wheaton glass-stopped lidded reagent bottles - 50 ml, 150 ml.

b. GC Instruments and Analysis Parameters Used.

(1) Gas Chromatographs

(a) Tracor® MT-220.

(b) Tracor MT-222.

(c) Tracor 560.

(2) Detectors

(a) High temperature Ni^{63} electron-capture detector (EC) - used for detection of organochlorine pesticides, organophophorous pesticides and PCB's.

(b) Flame photometric detector operating in phosphorous mode (FPD) - used for detection of and confirmation of organophosphorous pesticides.

(c) Coulson electrolytic conductivity detector - used for confirmation of organochlorine pesticides.

(3) Gas Chromatographic Columns.

(a) 1.5 percent OV-17/1.95 percent QF-1 on 80/100 Gas ChromQ - used as primary screening and quantitation column with EC detector; used as a confirmatory column with FPD; used as primary column with Coulson electrolytic conductivity detector.

(b) 4 percent SE-30/6 percent SP-2401 on 100/120 SUPELCON AW-DMCS - used as confirmatory column with EC detector and Flame Photometric detector.

(c) 3 percent OV-1 on 100/120 Gas ChromQ - used as screening and quantitation column with FPD.

(d) 5 percent OV-210 on 80/100 Gas ChromQ - used as confirmatory column with EC detector.

(4) Recorder. Honeywell Electronik 194 or 196 Potentiometric Strip Chart (1 mV)

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(5) Routine Analysis Parameters for GC.

(a) Column oven temperatures: 195-205°C [used with columns 3(a) and 3(c)] 210°-215°C [used with column 3(b)] 180-185°C [used with column 3(d)].

(b) Injection port temperatures: Tracor MT-220 and MT-222 - 220-230°C (off-column injection used) Tracor 560-150° (on-column injection used).

(c) Detector temperature: EC-290°-310°C, FPD-200°-210°C; Coulson electrolytic conductivity detector - pyrolysis furnace (820°C); transfer line (240°C)

(d) Carrier gas flow: EC column (95% Argon - 5% Methane) 60-70 ml/min [used with columns 3(a) and 3(b) 45-50 ml/min [used with column 3(d)]; FPD columns (nitrogen) - 60 ml/min; Coulson electrolytic conductivity detector column (nitrogen) - 60 ml/min

(e) Detector gas flow: FPD - hydrogen (50 ml/min); zero air (90 ml/min): Coulson electrolytic conductivity detector

(f) Recorder speed: 0.5 in/min

(g) Electronics: EC detectors were operated in pulsed mode or pulsed linearized mode. FPD - operated with electrometer model No. 8169 Input 103; Output 4 or 8. Coulson electrolytic conductivity detector - Conductivity bridge settings, volts = 30; attenuator = 4 or 8

c. GC Quantitation Methods.

(1) Automatic Integration Method. Automatic integration of peak areas was carried out using an Auto Lab System IV Computing Integrator (Spectra-Physics, Mountain View, CA). This method was used for quantitation of most organochlorine pesticides peaks using EC detection.

(2) Manual (Peak Height Measurement) Method. This method of quantitation was used for all organophosphorous pesticide peaks using FPD, and for quantitation of organochlorine pesticide peaks using EC detection or those instruments not serviced by the Auto Lab System IV Computing Integrator.

d. GC Confirmation Techniques.

(1) Approximately 10 percent of routine positive GC pesticide results were confirmed by one or both of the GC confirmation techniques described below. In addition all unusual (i.e., quantitative or qualitative) pesticide results were confirmed if possible.

(2) GC results were confirmed by the following two techniques:

(a) Comparisons of retention times of sample pesticide peaks and reference standard peaks on one or more alternate chromatographic columns. Alternate columns used for confirmation of organochlorine pesticides and organphosphorous pesticides with EC and FPD detectors are listed in Part 4b(3) of this Appendix.

(b) Comparisons of retention times and detector responses for peaks and reference standard sample pesticide peaks using element specific GC detectors i.e., FPD for organophosphorous pesticides and Coulson Electrolytic conductivity detector for organochlorine pesticides.

Part 5. QUALITY CONTROL PROCEDURES.

a. Use of Standardized, Validated Published Analytical Methodology. Where available and feasible, standardized and validated published analytical methodology was used. A discussion of the sources of the analytical methodology employed in this study, as well as any procedural additions and/or modifications made in the methodology has been previously presented in Part 1 of this Appendix.

b. Use of Intralaboratory Spiked Reference Material (SPRM).

(1) Soil and Sediment. Intralaboratory SPRM samples to be used with soil and sediment analyses were prepared in-house by spiking a number of 150 g subsamples of composited soil (in 1-qt wide-mouth glass jars) with known concentrations of six different pesticides. Eight replicates of the SPRM sample were analyzed initially by experienced analytical personnel to establish essential baseline statistical data for quality control charts. The remaining SPRM samples were stored in a freezer until extraction and analysis. Approximately one SPRM sample was run for every 20 routine DAPMP soil and sediment samples.

(2) Fish and Birds. A supply of chicken fat, fortified with known amounts of six to seven pesticides and PCB's was received periodically from EPA, RTP, NC for use as intralaboratory SPRM samples for validation of fish and bird analyses. Approximately six replicates of each EPA chicken fat SPRM was analyzed initially by experienced analytical personnel to establish essential baseline, statistical data for quality control charts. The EPA SPRM was stored in a freezer when not in use. Approximately one EPA SPRM sample was run for every 10 routine DAPMP fish and bird samples.

c. Interlaboratory Quality Control. Analytical personnel of the Pest Management and Pesticide Monitoring Division/USAEHA responsible for the analysis of DAPMP samples actively participated in the interlaboratory quality control program of the EPA, Environmental Toxicology Division RTP, NC. This program involves analysis on a yearly basis of a blind interlaboratory check sample. Coordination of receipt of interlaboratory check samples from EPA and reporting of subsequent analytical results to EPA is affected by the Analytical Reference and Quality Assurance Division/USAEHA.

d. Glassware Decontamination Quality Control.

(1) All glassware used in the processing and analysis of DAPMP samples was soaked for a minimum of 4 hours in Chem Solv® biodegradable laboratory glassware cleaner prior to washing in a Forma-Fury Model 8698 (Forma Scientific, Marietta, OH) glassware washer.

(2) After washing and air-drying, representative glassware from each glassware load was rinsed with pesticide grade petroleum ether, and the rinses concentrated approximately 20 to 1 in a Kuderna-Danish apparatus. The concentrated glassware rinses were screened using EC detection for residual pesticide and other relevant contaminants prior to placing the glassware back into laboratory use.

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APPENDIX E

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APPENDIX F

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